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THE JOURNAL

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THE AMERICAN CERAMIC SOCIETY

Vol. 26 August 1, 1943 No. 8

EXPERIMENTS WITH AN ACCELERATED WEATHERING TEST FOR PORCELAIN ENAMELS*

By G. H. Spencer-Strong and W. G. Cooper

Abstract

Experiments were conducted on porcelain enamels using the accelerated weather test developed at the National Bureau of Standards. A comparison of results indicates this test to be a promising solution to the problem of the rapid determination of the weather resistance of porcelain enamel.

I. Introduction

The study of the weather resistance of porcelain enamels has been one of the most difficult tasks faced by the enameler. Experiments with accelerated tests in general have been unsuccessful.[1] Suppliers of enamels for architectural use and other enamel types designed for out-of-door use have been forced to depend chiefly on experience for guidance with actual exposure of the enamel to the weather as the only alternative test. Inasmuch as even the poorest porcelain enamel has comparatively high weather resistance, such experiments must be continued over long periods of time and, preferably, in several locations.

Harrison and Moore[2] have been making an extensive study of the weather resistance of porcelain enamels. In the course of their investigation, they discovered that very fine spalling of the surface is one of the factors in the failure of porcelain enamel when it is subjected to weathering. Further investigation showed that this spalling could be reproduced in the laboratory with an accelerated test. When the present writers were asked to give an accelerated weathering test to certain enamels, the Harrison and Moore procedure was tried. The tests proved to be so interesting that further investigation on a somewhat broader scale was inaugurated, and the results are presented here.

II. Method of Procedure

The procedure of the Harrison and Moore accelerated weathering test consists of immersing the test specimens for 17 hours in water through which a stream of CO_2 gas is continuously passed. The system at the same time is held under a slight pressure.† Following the immersion, the specimens are dried in an oven at 110°C.

The effect of this test on eight enamels was compared with data obtained on the same enamels after actual weathering exposure over a period of four to five years. Data were also obtained indicating the effect of a number of coloring oxides on the weathering resistance of a nonacid-resistant enamel. A preliminary study, moreover, was made to determine the cause of the spalling phenomena.

III. Data and Results

(1) Comparison of Atmospheric and Accelerated Weathering

The effect of atmospheric and accelerated types of weathering was compared on black, white, and blue acid-resistant and nonacid-resistant enamels. The colorant in each case was smelted in the enamel frit. Actual atmospheric weathering tests were carried on for five years in a residential suburb of Baltimore, Maryland. Table I shows the behavior of the enamels under both tests.

The spalling defect described by Harrison and Moore[2] was noted on all but one of the enamels. Two general types of spalling were found, namely, (*a*) a coarse, heavy spalling somewhat similar to the defect known as

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 22, 1942 (Enamel Division). Received May 27, 1942; revised copy received March 25, 1943.

[1] M. G. Ammon, "Accelerated Weathering Tests on Porcelain Enamels," *Enamelist*, **12** [9] 8–10 (1935); *Ceram. Abs.*, **14** [9] 209 (1935).

[2] W. N. Harrison and D. G. Moore, "Weather Resistance of Porcelain Enameled Iron Structural Units," *Jour. Research Nat. Bur. Standards*, **28** [6] 735–55 (1942); R.P. 1476; *Ceram. Abs.*, **21** [10] 209 (1942).

† Harrison and Moore recommend a gas flow of 1 to 2 mm. per minute and a pressure of approximately 4 in. of mercury.

TABLE I

COMPARISON OF ACTUAL AND ACCELERATED WEATHERING

Enamel No.*	Type enamel	Test	Type of spalling	Gloss
1	Black non-AR†	Actual	Very bad, coarse	Very slight decrease
1	" "	Accelerated	Bad, coarse	" " "
2	" "	Actual	Fairly bad, fine	Reduced but not destroyed
2	" "	Accelerated	" " "	" " " "
3	Black AR	Actual	Very fine, giving appearance of scum‡	No change
3	" "	Accelerated	Very fine‡	" "
4	White AR	Actual	No visible attack	" "
4	" "	Accelerated	" " "	" "
5	White non-AR	Actual	Visible surface attack, slight coarse	Gloss decreased
5	" "	Accelerated	Visible surface attack, slight coarse	" "
6	Blue non-AR	Actual	Both fine and coarse	Gloss greatly decreased
6	" "	Accelerated	Very heavy, both fine and coarse	Gloss destroyed
7	" "	Actual	Heavy spalling, both fine and coarse	Gloss almost destroyed
7	" "	Accelerated	" " " " " "	Gloss destroyed
8	" "	Actual	Slight coarse, some fine, scummy appearance	Gloss decreased
8	" "	Accelerated	Slight coarse and heavy fine	Reduced from full gloss to semimat

* Frits used in milling enamels Nos. 1, 2, 6, 7, and 8 were of different composition; colorant was smelted into the frit in each case.
† AR, acid resistant.
‡ Not noticeable except under close study.

shiner scale and readily visible to the naked eye, and (*b*) a fine, microscopic type, somewhat like scumming to the casual observer but readily apparent as spalling under the microscope. The behavior of the enamels, moreover, was quite different. Enamels Nos. 1 and 5 showed only the coarse spalling; enamels Nos. 2 and 3, only the fine spalling; enamels Nos. 6, 7, and 8, both types; and enamel No. 4, no attack. The test results of the enamels under the two tests were generally the same.

Table II shows a comparison of the severity of attack in the two tests. Enamels Nos. 1, 2, and 3 showed less attack under the accelerated weathering than under the actual weathering; the results were similar for both tests on enamels Nos. 4 and 5, and enamels Nos. 6, 7, and 8 showed much more severe attack under the accelerated test than under actual weathering conditions.

TABLE II

COMPARISON OF SEVERITY OF ATTACK

Enamel No.	
1	Much less severe in accelerated test
2	Slightly less severe in accelerated test
3	" " " " " "
4	Same, no attack
5	Similar
6	Accelerated test much more severe
7	" " " " "
8	" " " " "

Results of the investigation indicate the possibility of a qualitative prediction of the comparative resistance to weathering of enamels by means of the accelerated test. Because of the many factors involved, however, a quantitative prediction has not been possible. The results of some of the actual and accelerated tests were surprisingly similar, whereas a considerable difference in degree of attack was noted in others. In each case, however, regardless of the comparative severity of the attack, the type of attack was the same.

(2) Effect of Coloring Oxides on Accelerated Weathering

The effect of accelerated weathering of various coloring oxides was determined by milling 3% of each oxide with a nonacid-resistant, clear frit with 5% of clay and 4 ounces of magnesium carbonate. The oxides used were a cobalt black, two cobalt-free blacks of different composition, a light blue, a medium blue, a brown, and a bright red. The red oxide was also added to a clear, acid-resistant frit. The same nonacid-resistant enamel frit was used throughout the experiments.

In the case of the cobalt-free black oxides, oxide No. 1 was reported to be much more stable during firing than oxide No. 2. The results of the test are shown in Table III.

The mill-added oxides in the nonacid-resistant enamels exert considerable effect on the resistance to accelerated weathering. The only acid-resistant enamel included in this test showed no attack, whereas a considerable degree of attack occurred on the nonacid-resistant enamel in which the same coloring oxide was used. A wide divergence in the amount of attack between the oxides was also noted. Enamel B, which consisted of a clear, nonacid-resistant enamel containing No. 1 cobalt-free black oxide, showed some attack but was not affected nearly so badly by the test as enamel C, which contained No. 2 cobalt-free black oxide, or enamel D, which contained a light blue oxide. The gloss was entirely destroyed in enamels C and D.

These experiments indicate definitely that mill-added oxides may be expected to exert considerable influence on the degree of weather resistance, especially in nonacid-resistant enamels.

(3) Effect of Bubble Formation on Spalling

In order to study the mechanism of spalling, which was noted in the accelerated weathering test, the effects of various clays and opacifiers giving rise to vari-

TABLE III

EFFECT OF COLORING OXIDES ON ACCELERATED WEATHERING

Test	Type enamel	Type of oxide	Type of spalling	Gloss	Comparison of residual gloss
A	Clear non-AR	Cobalt black	Much fine and a little coarse	Badly attacked	4
B	" "	Cobalt-free black No. 1	Much fine and a little coarse	Gloss somewhat reduced	2
C	" "	Cobalt-free black No. 2	Very heavy fine and considerable coarse	Full mat	7
D	" "	Light blue	Very heavy fine no coarse	" "	8 (poorest)
E	" "	Medium blue	Some fine	Better than semimat	3
F	" "	Brown	Considerable coarse and much fine	Almost mat	6
G	" "	Bright red	Very slight coarse	Badly reduced, mirror image just visible	5
H	Clear AR	" "	No attack	No change	1 (best)

ous types of bubble formations were investigated: A black nonacid-resistant enamel (No. 1, Table I) was milled with 5% of a bubble-producing clay and 5% of a so-called clear clay with a low bubble formation.

The same enamel was also milled without clay, and suspension was obtained by the addition of 0.5% of bentonite. The spalling in each case increased as the number and size of the bubbles in the enamel decreased. The enamel containing the bubble-producing clay thus showed a slight, coarse spalling with little decrease of gloss; the sample with the clear clay showed a greatly increased amount of spalling and a slight reduction in gloss. The enamel milled without clay showed heavy spalling of coarse and fine types as well as complete destruction of gloss.

When the bubble-producing clay and the clear clay, respectively, were milled in a clear, acid-resistant enamel (enamel H, Table III), the sample containing the bubble-producing clay showed no attack whereas the specimen milled with the clear clay again showed a marked increase in attack of coarse and fine spalling and a decrease in gloss.

When 3% of a bubble-producing opacifier was introduced into an acid-resistant enamel (enamel H, Table III) containing a clear clay, the fine spalling was slightly increased. No attack occurred, however, when a bubble-free opacifier was used.

These data indicate the importance of clays in weather resistance, but they show no direct correlation between bubble formation and weathering. An examination of a weathered enamel surface under a low-power microscope indicated that the spalling and bubble patterns are identical in many instances.

(4) Experiments with Blue Enamels

In view of the excessive attack by the accelerated weathering test on the blue enamels as shown in Table I, further experiments were made on three acid-resistant enamels and one nonacid-resistant blue enamel. The color oxide was smelted into the frit in each sample. The acid-resistant blue enamels were not attacked to any appreciable degree, but all of the nonacid-resistant enamels showed marked attack to a degree similar to that shown by enamels Nos. 6, 7, and 8 (Table I).

When blue oxides were used in enamels D and E (Table III), enamel D showed very heavy attack whereas the attack was less severe on enamel E. One of the eccentricities of the accelerated weathering test that must be corrected in order to obtain better correlation with actual atmospheric weathering effects is the tendency to exaggerate the weathering of blue types of enamels. Although the black types of enamels showed less severe attack than is found in actual weathering tests, the degree of attack on the blue enamels was much greater in the accelerated tests than under actual exposure conditions.

IV. Conclusions

Although the data obtained are inadequate to form a definite theory relating to the mechanism of the accelerated weathering tests, the heavy spalling often appears to involve large bubbles or close clusters of small bubbles. When a few bubbles appear, the spalling often follows a bubble pattern. When scumming or shorelining defects occur in a few samples, the spalling appears to follow the pattern of these defects.

This investigation shows that the use of the Harrison and Moore accelerated weathering tests is simple, comparatively rapid, and foolproof. The writers believe that the accelerated tests should give a basis for prediction of the general behavior under actual weathering conditions. The operator of the test should be able to predict whether a particular type of enamel is more susceptible to weathering than a similar type of different composition. He should also be able to indicate in general whether an enamel will be affected by atmospheric weathering and the comparative weather resistance of one enamel with another. In its present state of development, however, this test does not permit a prediction of the degree of weather resistance of various porcelain enamels.

PORCELAIN ENAMEL AND MANUFACTURING COMPANY
BALTIMORE, MARYLAND

SUBSTITUTION OF TOPAZ, DOMESTIC KYANITE, AND SYNTHETIC MULLITE-CORUNDUM FOR INDIA KYANITE, I–III*

By T. N. McVay and Hewitt Wilson†

Abstract

This report on the utilization of domestic materials as replacements for India kyanite has been divided into four parts, namely, (I) kyanite and other high-grade refractories, (II) effect of heat on kyanite and topaz, and (III) load resistance of refractories at elevated temperatures; (IV) will be published later.

PART I. KYANITE AND OTHER HIGH-GRADE REFRACTORIES

I. Introduction

Refractories made from India kyanite have comparatively high melting points, constancy of volume under service conditions, and resistance to loads at high temperatures and to thermal shock.

The more important commercial uses include (1) linings for Ajax-Wyatt induction and indirect arc furnaces for melting and refining brass and bronze containing more than 75% of copper and those metals that require higher temperatures than does yellow brass, (2) furnaces in which silica brick can be used for continuous service but spall during intermittent operation, (3) oil-burner ports and blocks, (4) superstructure for glass tanks exclusive of the silica-brick crowns, including the forehearth and mechanical feeder parts for forming machines and (5) heavily loaded kiln furniture for fast schedules in ceramic firing. Heuer[1] has given a more complete discussion of the use of India kyanite refractories.

II. Occurrence and Properties of India Kyanite

The principal known commercial deposit of India kyanite occurs at Lapsa Buru (hill), Singhbhum, Khwarsan State, which is about 100 miles west of Calcutta. Deposits in Burma have also been reported in use.

Massive kyanite is associated with quartz-kyanite rock at or near Lapsa Buru, as shown in the map by Dunn,[2] Fig. 1. Some topaz-granulite also occurs at Lapsa Buru, and occasional lumps are found with the American imports of kyanite. According to the latest information available, the kyanite has been mined from the detrital deposits, which are undoubtedly the weathered residues from less-resistant rocks. For the most part, the kyanite is massive and usually contains some corundum, which may run as high as 85%. No quartz was found in any of the samples. According to Dunn,[2] at least 210,000 tons of kyanite are available, and there may be ten times this amount.

Like all kyanites, India kyanite expands when heated, but it also produces a hard grog with a minimum amount of fines. The calcined domestic kyanite concentrates from the known deposits are soft and friable. Some specimens of India kyanite are massive, and others consist of long fibrous crystals, but each produces a better consolidated grog than the domestic mineral.

India kyanite is an excellent material for refractories because of the following properties: (1) It has a high refractoriness as shown by the P.C.E. (cones 37 to 39); (2) it contains a high alumina content (56 to 92%) and usually free corundum beyond the theoretical kyanite requirement of 62.9% of alumina; (3) it may be calcined to a hard mass suitable for use as a coarse grog; grog made from the better grades of India kyanite is practically volume constant when reheated from 1400° to 1700°C; (4) it may be manufactured into large, complicated shapes with a small amount (15%) of plastic or flint clays and, with normal firing, produce products with 15 to 20% of apparent porosity; and (5) it has excellent load resistance at high temperatures.

Importations of India kyanite since 1937 have been 7674 tons in 1937; 3964 tons in 1938; 3381 tons in 1939; and 7658 tons in 1940.

(1) Replacement of India Kyanite by Domestic Materials

The domestic materials that may be considered as possible substitutes for India kyanite are domestic kyanite, South Carolina topaz, California andalusite with diaspore, diaspore clays, electric-furnace mullite-corundum, and low- and high-grade bauxite.

Except for bauxite and electric-furnace corundum made from high-grade bauxite, only a small portion of the reserves of the foregoing materials listed is needed at the present time to produce goods necessary for the war. Electric-furnace products, however, utilize power and equipment, which in certain districts are needed for other purposes.

III. Domestic Kyanite

Four areas in the United States are producing

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† The authors are, respectively, senior ceramic engineer and supervising engineer, Electrotechnical Laboratory, Bureau of Mines, U. S. Department of the Interior, Norris, Tenn.

[1] R. P. Heuer, "Kyanite Refractories," *Brick & Clay Record*, **100** [3] 50–51 (1942); *Ceram. Abs.*, **21** [8] 171 (1942).

[2] J. A. Dunn, "Aluminous Refractory Materials: Cyanite, Sillimanite, and Corundum in Northern India," *Geol. Surv. India, Memoirs*, **52** [2] 145–274 (1929); *Ceram. Abs.*, **9** [3] 201 (1930).

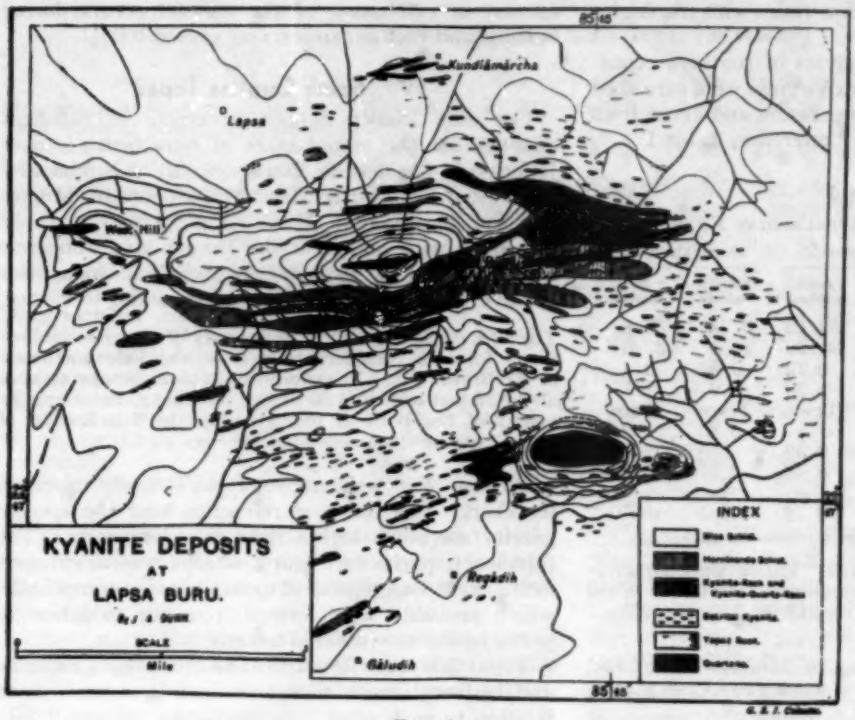

FIG. 1.

kyanite. The Kyanite Products Corporation[3] has a mill at Darlington Heights in Prince Edward County near Pamplin, Va. According to Sawyer and Whittemore,[4]

> The kyanite of the Baker Mountain deposit contains a massive-type kyanite-quartzite, which occurs abundantly, and also small needlelike masses of radiating kyanite crystals in quartzite. The schist includes small amounts of rutile, hematite, pyrite, and quartz, most of which are eliminated by the concentration process and by magnetic separation. The kyanite occurs as deep greenish blue bladelike crystals.

The Yancey County Cyanite Company, formerly known as Celo Mines, Incorporated, has a mill on Celo Mountain near Burnsville, Yancey County, N. C. The principal ore deposit has been described by Mattson[5] with details of the kyanite-recovery process. It is a huge lens of kyanite gneiss, which has been outlined definitely by systematic sampling. According to the Bureau of Mines, several million tons of ore averaging 11% of kyanite and 8% of garnet are available. Mattson[6] has pointed out that most of the kyanite must be obtained from rock having crystals disseminated in schist rather than from massive kyanite deposits inasmuch as the latter deposits are small and widely separated.

The A. P. Green Fire Brick Company of Mexico, Mo., mines kyanite near Clarkesville, Ga. The kyanite occurs in schist and placer deposits. Boyd[7] has described the recovery from the schist, and Greene,[8] the winning of the kyanite from the placer deposits.

The Vitrefrax Corporation of Los Angeles, Calif., has a kyanite deposit near Ogilby, Imperial County, Calif.[9]; this mine is operated by the American Minerals Company, which also does the milling. According to Sampson and Tucker,[9]

> The deposit of kyanite occurs at the foot of the Cargo Muchacho Mountains. It is one-eighth mile in width, and its outcrop can be traced one mile in length. The rock is reported to consist of 25% of kyanite in a matrix of quartz. Five thousand tons of ore mined from the deposit are reported to contain 40% of kyanite.

Other possible commercial deposits have been reported at other locations in North Carolina, at Knob Hill, S. C.,[10] and at Graves Mountain, Ga.[11] Deposits, probably of no commercial importance, have been reported from Alabama,[12] Maryland, Pennsylvania, Wyoming, southern Idaho, and California.[10] Kyanite at one time was mined in New Mexico.[13]

An abundant supply of domestic kyanite, therefore, is available, but the largest known reserves are in the southern Appalachian Mountains.

(*A*) *Chemical Analysis:* Domestic kyanite prepared for the market always contains excess silica and other

[3] Minerals Yearbook (review of 1940). U. S. Bureau of Mines, Govt. Printing Office, Washington, D. C., 1941. 1456 pp.; *Ceram. Abs.*, **20** [11] 272 (1941).

[4] J. P. Sawyer, Jr., and J. W. Whittemore, "Characteristics of Virginia Kyanite," *Bull. Amer. Ceram. Soc.*, **19** [12] 459–61 (1940).

[5] V. L. Mattson, "Kyanite Operations of Celo Mines, Incorporated," *ibid.*, **15** [9] 313–14 (1936).

[6] V. L. Mattson, "Progress in Commercial Development of Kyanite in the South Atlantic States," *ibid.*, **13** [9] 226–28 (1934).

[7] W. B. Boyd, "Recovery of Kyanite from North Georgia Schist," *Bull. Amer. Ceram. Soc.*, **19** [12] 461–63 (1940).

[8] C. F. Greene, "Placer Mining Kyanite in Georgia," *Brick & Clay Record*, **86** [4] 131 (1935); *Ceram. Abs.*, **14** [7] 166 (1935).

[9] J. R. Sampson and W. B. Tucker "Mineral Resources of Imperial County, State of California," *Dept. of Natural Resources, Div. of Mines, Calif. Jour. Mines and Geol.*, **38** [4] 105–45 (1942).

[10] Industrial Minerals and Rocks. Edited by S. H. Dolbear, Amer. Inst. Mining Met. Eng., New York, 1937; Maple Press Co., York, Pa. 955 pp.; *Ceram. Abs.*, **17** [11] 364–65 (1938).

[11] J. H. Watkins, "Kyanite in Graves Mountain, Georgia," *Bull. Amer. Ceram. Soc.*, **21** [7] 140–41 (1942).

[12] Edgar Bowles, "Kyanite in Eastern Alabama," *ibid.*, **18** [8] 316 (1939).

[13] Minerals Yearbook (review of 1938). Bureau of Mines, Govt. Printing Office, Washington, D. C., 1939 1447 pp.; *Ceram. Abs.*, **19** [1] 28 (1940).

impurities, and the composition varies with the degree of beneficiation of the ore.

Table I shows typical analyses of southern Appalachian kyanites; those from Virginia were furnished by the Kyanite Products Corporation and those from North Carolina by Pole (see * reference, Table I).

TABLE I

ANALYSES OF SOUTHERN APPALACHIAN KYANITES

	Virginia		North Carolina	
	Regular	Acid leached	80–40-mesh	−100-mesh
Al_2O_3	58.77	59.13	57.4	59.8
SiO_2	37.70	38.20	40.4	37.3
Fe_2O_3	1.17	0.32	0.5	0.4
TiO_2	1.30	1.20	0.9	1.1
MgO	Trace	Trace	Trace	Trace
CaO			0.8	1.2
K_2O and Na_2O	0.59	0.39	..	..
Ignition loss	0.38	0.48	0.1	0.2
	99.91	99.72	100.1	100.0
P.C.E.	36–37			

* G. R. Pole and D. G. Moore, "Expansion Characteristics of Kyanite and Kyanite-clay Mixtures When Heated," *Bull. Amer. Ceram. Soc.*, 17 [9] 355–67 (1938).

(*B*) *Production:* According to Minerals Yearbook, Review of 1940,[3] 4241 short tons of kyanite valued at slightly less than $94,000 f.o.b. mines were shipped in 1940 compared with 2950 short tons valued at $69,000 f.o.b. mines in 1939. California and Virginia were the leading producing states.

(*C*) *Pyrochemical and Pyrophysical Changes in Kyanite, Sillimanite, and Andalusite:* According to Peck,[14] kyanite dissociates into mullite at about cone 12 as compared with andalusite at cone 13, but sillimanite does not break down even at cone 15. Greig[15] has pointed out that

> The lowest temperatures at which alterations take place are different for the three minerals. Kyanite alters at the lowest temperature and sillimanite at the highest. For all three, there is no definite temperature at which the mineral decomposes sharply to the new phases and below which it remains unaffected for an indefinitely long period.

The rate of inversion, however, is comparatively rapid for kyanite at 1335°C., andalusite at 1530°C., and sillimanite at 1650°C. The three minerals are decomposed on heating to mullite and silica or to mullite and siliceous liquid. The silica probably is cristobalite.

All of these have a volume expansion when heated, but it is small for andalusite and sillimanite. Based on the true specific gravity of raw (3.59) and of calcined (3.09) kyanite however, the calculated volume expansion of kyanite is 16%. This is much less than the actual bulk-volume expansion because a large amount of exfoliation of the mineral occurs during heating, and such expansion may exceed 100%.

IV. South Carolina Topaz

The only known deposit occurring in sufficient quantity for the manufacture of refractories is near Jefferson in Chesterfield County, S. C.; it is mined by the United Feldspar & Minerals Corporation, Minpro Division, Spruce Pine, N. C. The presence of topaz associated with quartz at the Brewer gold mine was first suspected by Graton[16] in 1906, and topaz was positively identified by Pardee.[17] According to Pardee,

> The rock consisting almost exclusively of very fine-grained topaz forms a considerable part of the lode northwest of the Brewer pit. The exposures in place occupy an area about 25 feet wide and 50 feet or more long, but a greater extent of the body is indicated by the distribution of "float" on the slope above the outcrop.

Because of its appearance, topaz is easily mistaken for chert. The index of refraction and the specific gravity are much higher than those of quartz. The principal impurities are quartz, which occurs as stringers in the crystal aggregates of topaz, and iron compounds, which probably were formed from the oxidation of pyrite in the unweathered mineral.

Topaz has the formula $Al_2SiO_4(F\text{-}OH)_2$. Fluorine and hydroxyl are isomorphous and thus variable in relation to each other. According to Burgess,[18] SiF_4 and HF are driven off when topaz is heated. Bradley, Schroeder, and Keller[19] report that about 5% of the silica present in the original ore is removed through volatilization of the fluorides, and they give the critical temperature of calcination as 1260°C. after a 5-hour heating period. According to Pole,[20] the optimum conditions for calcination in an oil-fired rotary kiln 25 ft. long and with an inside diameter of 20 in. are rate of feed, 300 lb. per hour; feed retention time, 70 minutes; and temperature, about 1480°C. The conditions for calcination thus depend on time and temperature and probably on the grain size of the feed.

Stuckey and Amero[21] found mullite to be the principal constituent at 1000°C., and the mullite content increased as the temperature was raised. Bradley, Schroeder, and Keller[19] have reported complete mullitization at 1260°C.

The values for the chemical analyses of Brewer mine topaz are those given by Burgess[18] (see Table II).

[14] A. B. Peck, "Changes in Constitution and Microstructure of Andalusite, Cyanite, and Sillimanite at High Temperatures and Their Significance in Industrial Practice," *Jour. Amer. Ceram. Soc.*, 8 [7] 407–29 (1925).

[15] J. W. Greig, "Formation of Mullite from Cyanite, Andalusite, and Sillimanite," *ibid.*, 8 [8] 465–84 (1925).

[16] L. C. Graton, "Reconnaissance of Some Gold and Tin Deposits of the Southern Appalachians," *U. S. Geol. Surv. Bull.*, No. 293, 134 pp., 1906.

[17] J. T. Pardee, J. J. Glass, and R. E. Stevens, "Massive Low-Fluorine Topaz from Brewer Mine, S. C.," *Amer. Mineralogist*, 22 [10] 1058–64 (1937).

[18] B. C. Burgess, "Topaz Development as Source of Alumina," *Bull. Amer. Ceram. Soc.*, 21 [7] 135–39 (1942).

[19] R. S. Bradley, F. W. Schroeder, and W. D. Keller, "Study of Refractory Properties of Topaz," *Jour. Amer. Ceram. Soc.*, 23 [9] 265–70 (1940).

[20] G. R. Pole, "Calcination of Topaz Ore in a Rotary Kiln," *Rept. No. 1, W.O. 5100, Dept. of Chemical Engineering, Tennessee Valley Authority*, 13 pp., April 15, 1942.

[21] J. L. Stuckey and J. J. Amero, "Physical Properties of Massive Topaz," *Jour. Amer. Ceram. Soc.*, 24 [3] 89–92 (1941).

TABLE II

ANALYSES OF BREWER MINE TOPAZ (BURGESS[18])

Description	Loss	SiO_2	Al_2O_3	Fe_2O_3	F_2	Subtotal	Less (O = 2F)	Total
Float material (first car shipped)	No data	40.20	50.28	0.92	12.74	104.14	5.37	98.77
Float material ground to 200-mesh at Staley (first lot)	1.51	42.80	48.62	0.98	11.93	105.84	5.03	100.81
Float material (10 tons) ground to 200-mesh at Staley (second lot)	1.24	39.60	51.30	0.70	12.65	105.49	5.33	100.16
Heavy gray vein material	1.08	39.30	52.34	0.16	12.73	105.61	5.37	100.24
Shipments of vein topaz (Oct., 1941)	No data	40.20	51.79	0.21	13.35	105.55	5.63	99.92
Float material (sample sent to N. C. State College)	" "	32.70	57.80	0.75	14.20	105.45	5.98	99.47
Float material (calcined by N. C. State College)	" "	29.85	69.22	0.82	0.12	100.01	0.05	99.96
Float material (calcined by Minpro Laboratory)	" "	28.90	71.06	0.22	0.15	100.33	0.06	100.27
Float material (30 tons) partially calcined at Pontiac, S. C.	" "	42.50	53.29	1.01	5.28	102.08	2.21	99.87
Vein topaz (15 tons to Sheffield for calcining)	0.88	37.20	53.25	0.35	14.10	105.78	5.90	99.88
Calcined vein topaz (Sheffield)	No data	32.50	67.30		0.31	100.11	0.12	99.99

The alumina to silica ratio of the calcined material from the Minpro Laboratory was 2.46 as compared with 2.55 for mullite, indicating that little excess silica was present.

Fries[22] states that the possible and probable amount of topaz available at or near the Brewer mine is 55,000 tons. Burgess[18] estimates that 260,000 tons of topaz may be available in the district.

V. Andalusite

The first commercial deposit of andalusite discovered in this country occurs in Mono County, Calif., at an elevation of 10,000 feet on the west slope of White Mountain of the Inyo Range, near the small town of Laws. The deposit was opened by Champion Sillimanite, Incorporated, a subsidiary of the Champion Spark Plug Company of Detroit, Mich. This deposit has been worked for about twenty years. The geology and mineralogy of the deposit have been fully described by Peck.[23]

Generally the material runs at least 75 to 85% of andalusite on microscopic examination. A typical analysis from a sample representing a carload shipment, recalculated to an Al_2SiO_5 basis, will show over 90% of Al_2SiO_5.

Analysis		Equivalent to	
SiO_2	33.78	Al_2SiO_5	94.18
Al_2O_3	56.89	SiO_2	0.22
H_2O	0.37	Other	5.60
Ignition loss	3.67		
Other	5.37		

The fact that the chemical analysis generally shows higher Al_2SiO_5 than is indicated by the microscopic examination is due to the frequent occurrence of corundum in the material.

The principal accessory minerals associated with the andalusite are lazulite, pyrophyllite, muscovite, and corundum.

Champion-Sillimanite, Incorporated, has opened New Camp mine* on the west slope of White Mountain in Mono County, Calif. (almost on the border between California and Nevada), approximately 7000 to 8000 feet above sea level and about four miles from the Southern Pacific Railway; a truck can be driven within two miles of the mine. This deposit is more accessible than the upper deposit.

The P.C.E. of andalusite is about cone 37. A petrographic analysis* of several samples showed that the average contents are andalusite 66.5%, diaspore and corundum 20.0%, rutile 4.0%, and mica and pyrophyllite 9.5%. The diaspore is well crystallized. Preliminary results indicated that this material is satisfactory for the manufacture of refractories.

The Tillotson Clay Products Company[24] of Los Angeles, Calif., has started mining andalusite near Hawthorne, Mineral County, Nev. This deposit is said to contain some diaspore and corundum. Mineral County, Nev., adjoins Mono County, Calif., but the deposits are some distance apart.

Twells[25] did some of the earliest work on the use of andalusite and found that refractories made from it were resistant to thermal shock, volume-constant, and had excellent load-bearing characteristics at high temperatures. Most of the tonnage mined by Champion-Sillimanite, Incorporated, from the old mine, however, has been used in the manufacture of spark-plug insulators.

According to Minerals Yearbook of 1940,[3] 400 to 2000 tons of andalusite and dumortierite have been mined annually, but there was no production of andalusite from Champion-Sillimanite, Incorporated, in 1940, and no prices were listed for the andalusite ore.

Although andalusite has been made into excellent

[22] Carl Fries, Jr., "Topaz Deposits near Brewer Mine, Chesterfield County, S. C.," *U. S. Geol. Surv. Bull.*, No. 936-c, pp. 57–78, 1942; *Ceram. Abs.*, **21** [11] 247 (1942).

[23] A. B. Peck, "Note on Andalusite from California, New Use and Some Thermal Properties," *Amer. Mineralogist*, 9, 123–29 (1924); *Ceram. Abs.*, **3** [10] 294 (1924).

* F. H. Riddle, Champion Spark Plug Co., Detroit, Mich., private communication.

[24] Minerals Yearbook, 1938 (review of 1937), p. 1305. U. S. Bur. Mines, Govt. Printing Office, Washington, D. C., 1938. 1339 pp.; *Ceram. Abs.*, **17** [11] 365 (1938).

[25] Robert Twells, Jr., "Progress Report on Use of Andalusite as a Refractory," *Jour. Amer. Ceram. Soc.*, **8** [8] 485–92 (1925).

refractories that can be substituted for India kyanite, the use of andalusite-diaspore probably will be restricted in the eastern part of the United States during the war on account of cost and transportation difficulties. Champion New Camp andalusite-diaspore, however, should be a valuable raw material for the production of refractories on the West coast.

VI. Electric-Furnace Mullite-Corundum

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is the only stable high-temperature crystalline aluminum silicate formed when any of the aluminum silicate minerals, such as andalusite, kyanite, sillimanite, topaz, dumortierite, or kaolinite, are heated to a sufficiently high temperature.

The Corhart Refractories Company has been manufacturing electric-furnace mullite-corundum for a number of years. It is produced by electric arc-resistance fusion of the proper combination of highly aluminous materials, such as bauxite, diaspore, or burley fire clays.

The molten mullite-corundum is cast into shapes that are annealed by slow cooling. These are used mainly for glass tank block and for other glasshouse refractories where erosion is particularly severe. With this casting process, a small tonnage of waste material is produced and is crushed and sized for the manufacture of bonded refractories. Because the mullite-corundum is cooled slowly, large crystals develop, consisting of a mixture of mullite and corundum with interstitial glass.

Inasmuch as suddenly cooled silicate melts are unstable and will devitrify in the proper temperature range, it was thought that such material might act as a high-temperature bond and furnish a continuous crystalline network. A supply of the water-quenched refractory was obtained from the Corhart Refractories Company.

The microscopic examination made by the Bureau of Mines showed that the mullite crystals in the water-quenched Corhart material were long and feathery. After heating at 1700°C., the water-quenched refractory consisted of a network of fine mullite crystals and corundum whereas crystallization of the standard Corhart refractory remained unchanged with this treatment.

A 2300-pound mullite-corundum melt was made in an electric-arc furnace in the Electrotechnical Laboratory of the Bureau of Mines and was designated pig No. 2014. The raw materials were as follows:

	(%)
Arkansas bauxite*	49.6
Calcined bauxite†	19.1
Georgia kaolin	26.8
Carbon coke	0.7
Iron turnings	3.8
	100.0

* Republic Gandy No. 2: 9.8 SiO_2, 54.0 Al_2O_3, 5.9 Fe_2O_3.
† Republic: 24.5 SiO_2, 3.5 Fe_2O_3.

The melt was allowed to cool slowly. It consisted of well-crystallized mullite and corundum with a small amount of glass and was similar to the standard Corhart refractory. After crushing, sizing, and magnetic separation, it was used in refractory compositions. Table III shows the chemical analyses of the three electric-furnace mullite-corundums.

VII. Diaspore

According to Norton,[26] Missouri diaspore consists of diaspore with kaolinite, silica, and impurities. The diaspore changes to corundum on heating between 550° and 950°C. and the kaolinite to mullite and silica at about 1000°C. At higher temperatures, the excess silica can react with corundum and form mullite. It is possible to obtain kyanite with the same chemical analysis as diaspore, but kyanite does not form corundum unless it is heated above the incongruent melting point; at this temperature, mullite dissociates into corundum and glass. On account of its structure, diaspore shrinks on firing and must be precalcined before it is incorporated into the refractory batch.

The volume stability of most diaspore refractories at temperatures above 1500°C. is inferior to that of India kyanite brick. Two of the leading manufacturers of diaspore refractories were unwilling to suggest diaspore as a complete replacement for India kyanite. One of these manufacturers makes both products. Diaspore can be changed into well-crystallized mullite and corundum by electric arc-furnace melting, but the the cost will be higher and the physical properties of the brick will not be the same as for those made from India kyanite because electric furnace mullite-corundum produces a very dense grog. The quantities of the best diaspore are reported to be limited.

VIII. Other Refractories

(*A*) *Fire Clay:* Even the best grades of fire clay have a much lower P.C.E. than kyanite and diaspore refractories and will deform under light loads at 1500°C. because of their comparatively low softening points. There is extensive variation among fire-clay refractories because a wide choice of materials is available as well as several methods of manufacture. These refractories may be designed to withstand service conditions, such as spalling, slagging, or moderate loads at elevated temperatures. From the standpoint of volume and sales, they are the most important of all refractories.

(*B*) *Silica:* The interlocking crystalline structure

TABLE III

ANALYSES OF ELECTRIC-FURNACE MULLITE-CORUNDUM*

	Bureau of Mines pig No. 2014 (%)	Corhart refractory (%)	
		Water quenched	Standard
SiO_2	21.3	21.6	21.0
Al_2O_3	73.9	72.0	72.2
TiO_2	2.8	3.3	3.4
Fe_2O_3	2.6	3.2	3.2
	100.6	100.1	99.8

* H. R. Shell, assistant chemist, Electrotechnical Laboratory.

[26] F. H. Norton, "Critical Study of Differential Thermal Method for Identification of the Clay Minerals," *Jour. Amer. Ceram. Soc.*, **22** [2] 54–63 (1939).

TABLE IV

QUOTATIONS (DECEMBER, 1942) ON REFRACTORY FIREBRICK*

High heat-duty fire-clay brick	$ 51.00–$ 55.00	
Superduty fire-clay brick	65.00– 87.00	
Diaspore (Al_2O_3, 50%)	86.50	
Diaspore (Al_2O_3, 60%)	110.50	
Diaspore (Al_2O_3, 60%), special	375.00	
Diaspore (Al_2O_3, 70%)	134.00	
Silica	51.00	
Silica (special)	61.00	(approx.)
Chrome ($54.00 per net ton)	300.00	"
Magnesite ($76.00 per net ton)	380.00	
India kyanite	500.00	
Bonded electric-furnace mullite	900.00	
Corundum (fused alumina, 90%)	900.00	
Silicon carbide (more than 85% of SiC)	1035.00	
Electrocast mullite-corundum, standard glass-tank shapes		$200.00 per ton

* Per thousand, standard 9- by $4^1/_2$- by $2^1/_2$-inch brick, carload lots, f.o.b. plant.

of the silica minerals and the very high viscosity of silica glass enable silica brick to withstand loads at high temperatures. Rapid heating or cooling through the range of room temperature to about 600°C. will cause spalling. Their porosity is also high, and they cannot withstand the slagging of many basic slags and glasses.

(*C*) *Magnesia:* Magnesia refractories cannot withstand the action of acid or aluminous fluxes, they fail under load at moderate temperatures, and they are not resistant to thermal shock. The addition of chromite improves their properties.

(*D*) *Chrome:* Chrome ore is scarce and is listed as a strategic mineral. The load-carrying properties of chrome refractories at high temperatures are poor, and they are not resistant to thermal shock. Except for carbon, however, they are the nearest to a chemically neutral refractory. The addition of magnesia improves their properties.

(*E*) *Bauxite:* Neither raw nor calcined bauxite has proved to be satisfactory for the manufacture of refractories. The shrinkage on firing is too great, and bauxite never becomes entirely volume-constant unless it is melted in an electric furnace and allowed to crystallize as corundum and mullite.

(*F*) *Silicon Carbide:* Silicon carbide refractories are characterized by high-heat conductivity and by excellent resistance to loads at high temperatures and to thermal shock; they have good slag resistance against coal ash and certain basic slags but oxidize slowly under some conditions. Silicon carbide, moreover, is expensive.

TABLE V

QUOTATIONS ON RAW MATERIALS

India kyanite	$38.00–$45.00
Domestic kyanite (raw kyanite, 35-mesh, 90%)	19.00
Calcined, 35-mesh bags	26.50
Raw, 200-mesh bags	26.50
Calcined, 200-mesh bags	31.50
South Carolina raw topaz	15.00
Corundum, refractory grade, 14-mesh bags	140.00
Electric-furnace mullite-corundum, 12-mesh bags	110.00
Silicon carbide, 14-mesh bags	150.00

IX. Cost of Refractories

Recent quotations on finished refractory products are shown in Table IV.

The prices of raw materials are shown in Table V. No prices are included for low-cost materials, such as fire clay, diaspore, or ganister. All prices are based on a net ton of 2000 pounds, carload lots, and f.o.b. plant or port of entry.

It is commercially feasible under certain favorable conditions to use high-cost raw materials for the production of brick to replace India kyanite refractories inasmuch as the selling price of the latter type is $500.00 per thousand standard 9-in. brick or about $110.00 per ton.

The best possibilities insofar as costs are concerned are topaz and domestic kyanite. It should be possible to calcine topaz and sell it at a price to compete with raw India kyanite. Domestic calcined kyanite is quoted at a price lower than India kyanite, f.o.b. port of entry. It is unlikely that electric-furnace mullite-corundum grog can be used unless it can be produced at about $50.00 per ton.

PART II, EFFECT OF HEAT ON KYANITE AND TOPAZ

IX. Constancy of Volume of Natural Mineral Specimens at Elevated Temperatures

The object of this part of the investigation was to determine the effect of high temperatures on the apparent porosity and volume change of natural samples of India kyanite, South Carolina topaz, and flint fire clay.

X. Description of Samples

(1) India Kyanite Samples

No. 1: Yellow, long, parallel fibers; some rutile crystallized with kyanite; no corundum noted.

No. 2: Extremely compact, massive, gray kyanite-corundum; intimate crystallization of kyanite with corundum, with more corundum present than kyanite.

No. 3: Red-brown; fibers radiated in all directions; many individual crystals longer than 1 mm.; rutile present; no corundum noted; color white after calcination of kyanite.

No. 4A: Yellow-brown; crystallized in radiating fibers, 2 mm. or more long.

No. 4B: Similar to No. 4A except kyanite occurred as long parallel fibers similar to No. 1.

No. 5: Extremely massive gray kyanite; no cleavage planes of the kyanite evident in thin section; small corundum crystals disseminated throughout kyanite.

No. 6: Massive and gray but not so compact as No. 5;

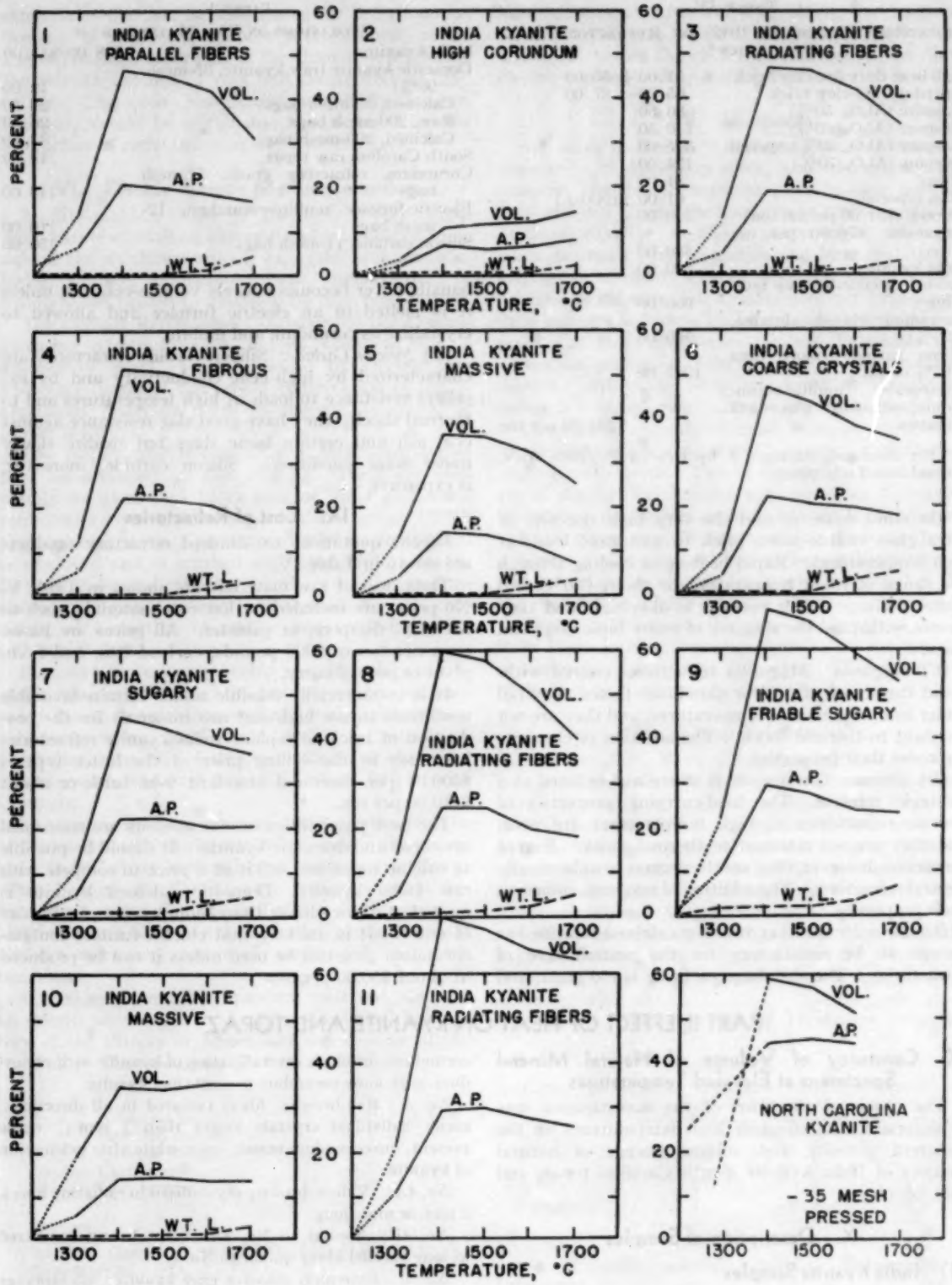

FIG. 2.—Repeated firings of identical samples.

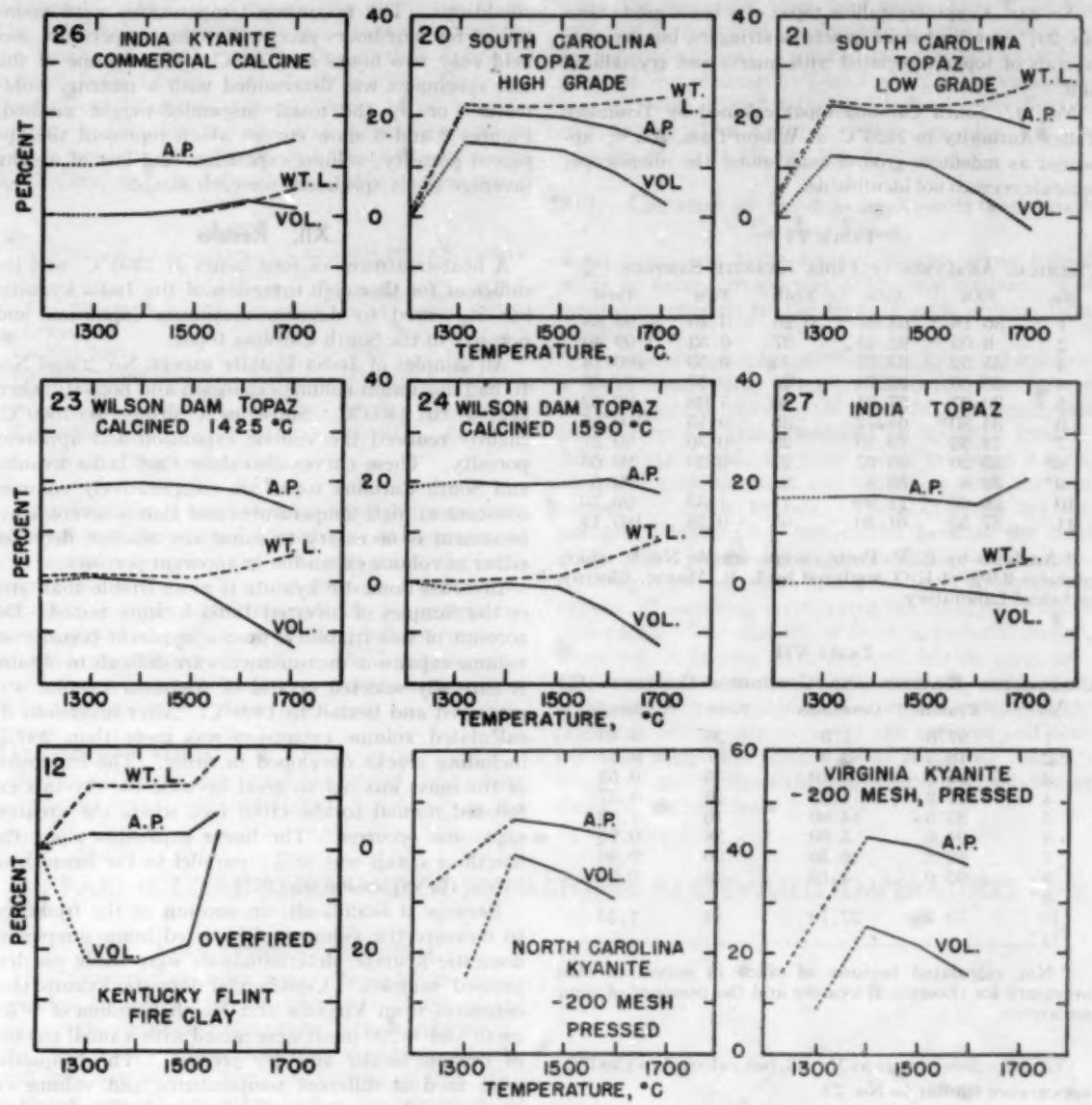

FIG. 3.—Repeated firings of identical samples.

mixture of coarse kyanite and corundum crystals; some corundum crystals 600 μ in diameter.

No. 7: Gray; compact but rather sugary in appearance because of large kyanite and corundum crystals.

No. 8: Gray; radiating kyanite crystals; cleavage planes of kyanite quite evident; rock easily crushed; no corundum noted; small amount of muscovite present.

No. 9: Bluish green and friable; individual crystals large and easily separated; small amount of corundum present as well as considerable muscovite.

No. 10: Very massive gray kyanite; rock exceptionally tough and difficult to crush; cleavage planes of kyanite, as seen in thin section, not well defined; corundum crystals disseminated throughout kyanite.

No. 11: Bluish green; kyanite crystals large with random orientations; crystals not well consolidated; rock easily crushed.

No. 26: Massive India kyanite, calcined by refractories manufacturer; before calcination, evidently similar to No. 10; corundum crystals disseminated throughout ground mass.

The chemical analyses of the India kyanite samples are given in Table VI, and the calculated corundum and mullite equivalents in Table VII.

(2) Topaz Samples

No. 20: Gray, very massive, high-grade S. C. topaz; cryptocrystalline with appearance of chert even when viewed with microscope at 270× magnification.

No. 21: Cryptocrystalline topaz of a lower grade than No. 20; contained some quartz as stringers, but separate crystals of topaz associated with quartz and crystallized in it.

No. 23: South Carolina topaz calcined by Tennessee Valley Authority to 1425°C. at Wilson Dam, Ala.[26]; appeared as indefinite ground mass under the microscope; separate crystals not identifiable.

TABLE VI

CHEMICAL ANALYSES OF INDIA KYANITE SAMPLES (%)*

No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Total
1	36.18	63.04	0.26	0.40	99.88
2	6.05	92.45	.37	0.53	99.40
3	35.52	63.73	.35	0.53	100.13
4	36.00	62.74	.29	0.57	99.60
5	30.97	67.31	.16	1.08	99.52
6	34.80	64.72	.38	0.15	100.05
7	19.32	79.39	.20	0.36	99.27
8	35.20	63.97	.23	0.30	99.60
9*	39.8	56.8	.8		99.8
10	26.05	71.99	.11	1.55	99.70
11	37.50	61.30	.63	0.58	100.13

* Analyses by E. P. Poste except sample No. 9, which contains 2.9% of K_2O, analyzed by L. R. Mason, Electrotechnical Laboratory.

TABLE VII

CALCULATED KYANITE AND CORUNDUM CONTENT (%)

No.	Kyanite	Corundum	Fe_2O_3	Rutile
1	97.6	1.5	0.26	0.40
2	16.3	82.0	.37	0.53
3	95.9	3.10	.35	0.53
4	97.2	1.53	.29	0.57
5	83.6	14.60	.16	1.08
6	94.0	5.60	.38	0.15
7	52.2	46.50	.20	0.36
8	95.0	4.10	.23	0.30
9*				
10	70.3	27.70	.11	1.55
11*				

* Not calculated because of silica in excess of that necessary for theoretical kyanite and the presence of some muscovite.

No. 24: Same topaz as No. 23, but calcined to 1590°C.; appearance similar to No. 23.

No. 27: Commercially calcined India topaz; one of few topaz lumps occasionally shipped with India kyanite; after calcination, lumps recognized by blistered surfaces; sample of unfired India topaz more coarsely crystalline than the domestic mineral.

(3) Fire-Clay Sample

No. 12: High-grade, Kentucky flint fire clay.

XI. Firing Natural Alumina-Silica Minerals

Six specimens were taken from each lump sample. This was advisable inasmuch as India kyanite is a heterogeneous rock and identical specimens are difficult to locate. The specimens were fired at 1300°C. and then progressively refired at 1400° and 1500° in a Globar kiln under oxidizing conditions. The 1600° and 1700°C. firings were made in graphite-resistor furnaces which operated under strongly reducing conditions. The maximum temperatures were maintained for four hours except that the temperature was held only two hours at 1700°C. The volume of the test specimens was determined with a mercury volumeter[27] or by the usual suspended-weight method. Figures 2 and 3 show curves which represent the apparent porosity, volume expansion, and loss of weight (average of six specimens for each sample).

XII. Results

A heat-treatment of four hours at 1300°C. was insufficient for thorough inversion of the India kyanite, but it served to develop maximum expansion and porosity in the South Carolina topaz.

All samples of India kyanite except No. 2 and No. 10 had maximum volume expansion and porosity when heated to 1400°C. Subsequent firing to 1500°C. slightly reduced the volume expansion and apparent porosity. These curves also show that India kyanite and South Carolina topaz are comparatively volume-constant at high temperatures and that a severe heat-treatment is necessary to cause any marked decrease either in volume expansion or apparent porosity.

Inverted domestic kyanite is more friable than any of the samples of inverted India kyanite tested. On account of this friability, precise apparent-porosity or volume-expansion measurements are difficult to obtain. A carefully selected crystal of Alabama kyanite was measured and heated to 1400°C. After inversion, its calculated volume expansion was more than 200%, including cracks developed in firing. The expansion of the mass was not so great because the crystals exfoliated normal to the (100) face where the greatest expansion occurred. The linear expansion along the length or *c* axis was 18%; parallel to the breadth or *b* axis, the expansion was 27%.

Because it is difficult, on account of the friability, to measure the volumes of inverted lump samples of domestic kyanite, determinations were made on dry-pressed samples. Commercial domestic kyanite concentrates from Virginia and North Carolina of −35-mesh and −200-mesh were mixed with a small amount of organic binder and dry pressed. The briquettes were fired at different temperatures, and volume expansion and porosity were determined (Figs. 2 and 3). The expansions of the −35-mesh samples were similar to those of the fibrous and radiating crystalline types of India kyanite; the briquettes were still soft at 1600°C., and the porosity was relatively high. The −200-mesh samples showed less expansion, greater strength, but similar porosity to that of the coarser sizes.

It is important to note that only the very massive varieties of India kyanite, namely, samples Nos. 2, 5, and 10, had lower porosity when fired at 1400°C. than the South Carolina topaz.

Table VIII gives the apparent porosity, bulk, and apparent specific gravity of samples of India kyanite selected from a large stock pile of a company processing India kyanite refractories. South Carolina topaz

[27] Sidney Speil and Hewitt Wilson, "Improved Mercury Balance Volumeter," *Jour. Amer. Ceram. Soc.*, **25** [No. 10, June 1] 275–77 (1942).

calcined to 1425°C. in a rotary kiln at Wilson Dam, Ala., is included for comparison. These data confirm the results of the laboratory firings that only the massive India kyanite has a lower porosity than calcined South Carolina topaz. Many India kyanite samples had higher porosity and volume expansion. This is mentioned because one of the criticisms of the South Carolina topaz is that its porosity is excessive.

TABLE VIII

PROPERTIES OF COMMERCIALLY CALCINED INDIA KYANITE AND TOPAZ

Description	Bulk sp. gr.	Apparent sp. gr.	Apparent porosity (%)
India kyanite			
Parallel fibers	2.47	3.05	18.4
Radiating fibers	2.47	3.09	19.4
High corundum content	3.42	3.88	11.8
Dense, massive	2.98	3.33	10.0
S. C. topaz,* 1425°C.	2.47	2.99	17.8

* Calcined at Wilson Dam, Ala.

Flint fire clay is used in high-heat and superduty refractories. The volume change and the porosity of lump samples heated in the same manner as the India kyanite samples are shown in Fig. 3. The volume shrinkage and porosity remained fairly constant between 1300° and 1500°C., but there was marked evidence of overfiring at 1600°C. The Kentucky flint fire clay consequently is not so volume-constant at high temperatures as kyanite and topaz.

(1) Loss of Weight

No loss of weight was found for any of the kyanite samples between 1300° and 1500°C. A loss occurred when the specimens were fired above 1500°C. in the load-test furnaces where graphite resistors gave a reducing atmosphere. As would be expected, topaz had a weight loss of about 21% as a result of the volatilization of water, silicon tetrafluoride, and other fluorine compounds. The Kentucky flint fire clay had an ignition loss of 14.2% at 1500°C.

XIII. Character of Fired India Kyanite and South Carolina Topaz

All topaz and India kyanite in this series turned white on firing, irrespective of the iron content. The corundum crystals in the kyanite rock became light grayish pink.

The massive samples of raw India kyanite furnished a hard, tough grog after calcination. The fibrous samples gave a friable grain, but this was much less friable than the grain produced by domestic kyanite. After firing, South Carolina topaz produced a grog comparable in hardness and toughness with the best samples of India kyanite. These qualities are important in processing refractories because the hard grain from kyanite and topaz produces a better load-resisting refractory than a soft exfoliated grain that is capable of shrinking on repeated heatings, particularly under load. The quantity of bonding material needed, moreover, is greater with the soft friable grog, particularly that made from the domestic kyanite whose cracked and fibrous structure requires a comparatively large amount of clay to cover the surfaces and thus bond the nonplastic portion of the refractory. A high bond content reduces the load-carrying resistance at elevated temperatures.

PART III, LOAD RESISTANCE OF REFRACTORIES AT ELEVATED TEMPERATURES

XIV. Load Resistance Properties

This property of refractories depends on many variables, including the constancy of volume of the grog and the softening points of both the bond and the grog. Secondary crystallization, shrinkage of the bond, and viscosity of the glass formed at high temperatures are likewise important. The structure of the brick contingent on the amount, size, and shape of the grog grains and the ratio of the plastic-to-nonplastic components must also be considered.

XV. Processing of Experimental Brick

The grog, bond clay, 1% of Marathon binder, and the proper amount of water were thoroughly mixed in a small Simpson mixer. The full-size brick were either dry pressed on the flat with a pressure of 7400 lb. per sq. in. or were formed by hand ramming in a metal slip mold. After drying, they were fired in a Globar test kiln to 1500°C. in about 24 hours (unless otherwise indicated in Table IX), and the temperature was held constant for four hours. Judging from the results of the tests, this firing procedure is believed to approximate the heat-treatment received by many similar refractories in commercial practice.

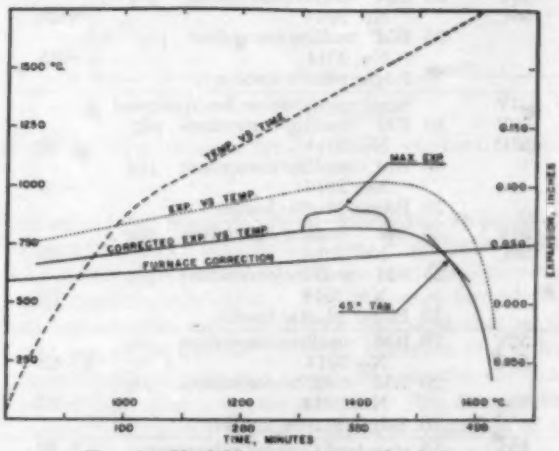

FIG. 4.—Variable temperature load test.

(1) Load Test Methods

The load test was used to evaluate the results obtained in processing materials that might be substituted for India kyanite. Two methods were used for conducting the tests, and these are designated as

TABLE IX

COMPOSITION (%) OF REFRACTORIES, BUREAU OF MINES (BM) TEST SPECIMENS

BM No.	India kyanite	Mesh
17V	55 calcined India kyanite*	8–28
	35 calcined India kyanite*	−35
	10 Edgar plastic kaolin	
BM No.	**South Carolina topaz**	
28V	55 topaz calcined by Carborundum Co.†	8–28
	35 topaz calcined by Carborundum Co.†	−150
	10 Champion and Challenger ball clay	
29V	Same as 28V‡	
30V	Same as 28V§	
31V	55 topaz calcined 1425°C., Wilson Dam, Ala.	8–28
34C	35 topaz calcined 1425°C., Wilson Dam, Ala.	−35
	10 Edgar plastic kaolin	
32V	55 topaz calcined 1590°C., Wilson Dam, Ala.	8–28
35C	35 topaz calcined 1590°C., Wilson Dam, Ala.	−35
	10 Edgar plastic kaolin	
33V	55 topaz calcined 1590°C., Wilson Dam, Ala.	8–28
36C	25 topaz calcined 1590°C., Wilson Dam, Ala.	−35
	10 raw topaz	−150
	10 Edgar plastic kaolin	
BM No.	**Andalusite, New Camp**	
37V	55 andalusite-diaspore	8–28
	35 andalusite-diaspore	−35
	10 Champion and Challenger ball clay	
BM No.	**Bonded electric-furnace mullite-corundum**	
46V	55 standard Corhart refractory	8–28
63C	35 standard Corhart refractory	−35
	10 Edgar plastic kaolin	
49V	55 BM mullite-corundum pig No. 2014	8–28
56C	35 BM mullite-corundum pig No. 2014	−35
	10 Edgar plastic kaolin	
103V	Same composition, hand pressed	
50V	50 BM mullite-corundum pig No. 2014	8–28
57C	40 BM mullite-corundum pig No. 2014	−35
	10 Edgar plastic kaolin	
51V	65 BM mullite-corundum pig No. 2014	8–28
58C	25 BM mullite-corundum pig No. 2014	−35
	10 Edgar plastic kaolin	
52V	70 BM mullite-corundum pig No. 2014	8–28
59C	20 BM mullite-corundum pig No. 2014	−35
	10 Edgar plastic kaolin	
53V	55 standard Corhart refractory	8–28
60C	25 standard Corhart refractory	−35
	10 calcined alumina	
	10 Edgar plastic kaolin	

BM No.	Bonded electric-furnace mullite-corundum (*concluded*)	Mesh
55V	55 BM mullite-corundum pig No. 2014	8–28
	25 BM mullite-corundum pig No. 2014	−35
	10 calcined diaspore	−100
	10 Edgar plastic kaolin	
BM No.	**Electric furnace mullite-corundum and topaz**	
66V	55 standard Corhart refractory	8–28
	35 topaz calcined 1590°C., Wilson Dam, Ala.	−35
	10 Edgar plastic kaolin	
68V	55 standard Corhart refractory	8–28
	25 topaz calcined 1590°C., Wilson Dam, Ala.	−35
	10 raw topaz	−150
	10 Edgar plastic kaolin	
69V	55 water-quenched Corhart refractory	8–28
	25 topaz calcined 1590°C., Wilson Dam, Ala.	−35
	10 raw topaz	
70V	55 BM mullite-corundum pig No. 2014	8–28
71C	35 topaz calcined Wilson Dam, Ala.	−35
	10 Edgar plastic kaolin	
104V	Same as 71C except hand pressed	
BM No.	**Electric-furnace mullite-corundum and domestic kyanite**	
79V	55 standard Corhart refractory	8–28
	35 Celo kyanite calcined at 1400°C.	−35
	10 Edgar plastic kaolin	
81V	55 standard Corhart refractory	8–28
	35 Celo kyanite calcined at 1400°C., recalcined at 1500°C.	−35
	10 Edgar plastic kaolin	
83V	55 BM mullite-corundum pig No. 2014	8–28
87C	35 Celo kyanite calcined at 1400°C., recalcined at 1500°C.	−35
	10 Edgar plastic kaolin	
105V	55 BM mullite-corundum pig No. 2014	8–28
	35 calcined Virginia kyanite	−35
	10 Edgar plastic kaolin	
106V	Same as 105V except hand pressed	
107V	50 BM mullite-corundum pig No. 2014	8–28
	35 calcined Virginia kyanite	−35
	15 Edgar plastic kaolin	
108V	Same as 107V except hand pressed	
BM No.	**Electric-furnace mullite, kyanite, and topaz**	
109V	30 BM mullite-corundum pig No. 2014	8–28
116C	30 raw Celo kyanite	−35
	30 raw topaz	35–80
	10 Edgar plastic kaolin	

* High-grade commercially calcined India kyanite.
† Preheated to 1650°C.
‡ Preheated to 1700°C.
§ Preheated to 1750°C.

‖ Grog, 90% of calcined Celo kyanite, −35 mesh, and 10% of Edgar plastic kaolin, pressed and fired at 1500°C.
¶ Fired in kiln at 1500°C., with topaz brick.

TABLE IX (*concluded*)

BM No.	Domestic kyanite	Mesh
101V‖	90 grog¶	
	10 Edgar plastic kaolin	
110V	90 calcined Virginia kyanite	−35
	10 Edgar plastic kaolin	

BM No.	South Carolina topaz and domestic kyanite	
96V	50 raw topaz	−8
	50 calcined Celo kyanite	−35
95V	45 raw topaz	20–80
102C	45 calcined Celo kyanite	−35
	10 Edgar plastic kaolin	
97V	45 raw topaz	8–35
	45 calcined Celo kyanite	−35
	10 Edgar plastic kaolin	
98V	45 raw topaz	−8
	45 calcined Celo kyanite	−85
	10 Edgar plastic kaolin	

BM No.	South Carolina topaz and domestic kyanite (*concluded*)	Mesh
111V	45 raw topaz	−8
	45 calcined Georgia kyanite	−8
	10 Edgar plastic kaolin	
112V	45 raw topaz	8–35
	45 calcined Virginia kyanite	−35
	10 Edgar plastic kaolin	
99V	45 raw topaz	−8
	22½ calcined Celo kyanite	−35
	22½ raw Celo kyanite	−35
	10 Edgar plastic kaolin	
113V	30 raw topaz	−8
114V	60 calcined Celo kyanite	−35
	10 Edgar plastic kaolin	
115V	10 raw topaz	−100
	80 calcined Virginia kyanite	−35
	10 Edgar plastic kaolin	

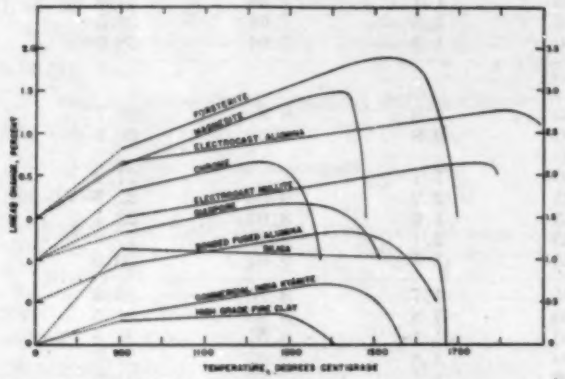

FIG. 5.—Variable temperature load test, commercial refractories.

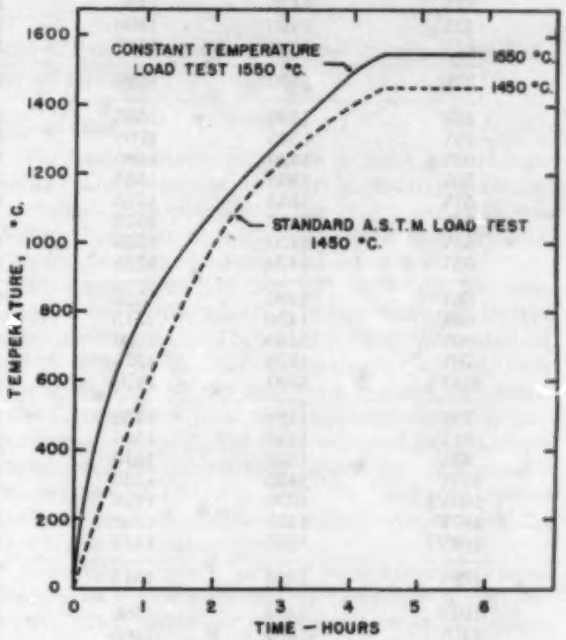

FIG. 6.—Time-temperature curves for constant temperature load tests.

the variable temperature (VT) and the constant temperature (CT) load tests.

XVI. Variable-Temperature Load Test

The load-test furnaces[23] developed at the Electrotechnical Laboratory at Norris, Tennessee, were used for this work. The temperature was gradually increased according to the schedule shown in Fig. 4, and the brick were subjected to a load of 25 lb. per sq. in. The expansion or contraction with the increase of temperature was measured; the linear change was plotted as the ordinate 1 in. equals 0.5%), and the temperature, as the abscissa (1 in. equals 100°C.).

A typical curve is shown in Fig. 4. To evaluate the results, the temperature at which maximum expansion occurred just before shrinkage started was taken as a critical point. With increased firing temperatures as the brick approached failure, the expansion curve dropped rapidly. As a measure of this rapid contraction, the temperature at which the slope of the expansion curve became 45° was considered critical. At temperatures above the 45° tangent, the contraction was exceptionally rapid. The difference between the temperature of maximum expansion and that at the 45° tangent is probably a good criterion of the load resistance of a refractory inasmuch as the shrinkage under load was not excessive over this temperature range. All curves were corrected for expansion of the furnace. Other pertinent data were recorded, such as linear contraction based on the length before testing, weight calculated to the volume of a standard 9-in. brick, and the percentage of porosity.

As the variable-temperature load test (V) is not in common use, typical commercial brick, such as superduty fire clay, silica, magnesite, chrome, forsterite, electro-

[23] (*a*) M. S. Nelson and R. R. Ralston, "Design and Operation of Electric Load-Test Furnace," *Jour. Amer. Ceram. Soc.*, **25** [No. 4, February 15] 112–16 (1942).
(*b*) Hewitt Wilson, "High-Temperature Load and Fusion Tests of Firebrick from Pacific Northwest in Comparison with Other Well-Known Firebrick," *ibid.*, **7** [1] 34–51 (1924).

TABLE X

VARIABLE TEMPERATURE LOAD-TEST RESULTS ON BUREAU OF MINES (BM) TEST SPECIMENS

	Temp., max. expansion (°C.)	Temp., 45° tangent (°C.)	Max. furnace temp. (°C.)	Linear shrinkage (%)	Standard brick wt. (lb.)	Porosity (vol. %)
			India kyanite*			
Avg.	1400	1486	1612	2.12	8.69	23.0
High	1490	1520	1730	4.70	9.14	25.0
Low	1310	1435	1540	1.00	8.23	20.0
BM No.						
17V	1480	1550	1670	1.0	8.80	24.8
			Topaz†			
Avg.	1380	1478	1586	2.20	8.31	24.3‡
High	1430	1500	1665	5.50	8.70	
Low	1315	1465	1507	1.20	8.12	
BM No.						
28V	1490	1550	1730	4.80	8.82	
29V	1535	1590	1755	4.9	8.95	
30V	1600	1630	1790	5.3	9.25	
31V	1420	1450	1595	1.4	7.56	31.3
32V	1420	1490	1610	1.5	7.66	29.5
33V	1430	1500	1610	1.5	7.94	28.0
37V	1470	1520	1650			
46V	1490	1535	1680	2.0	9.3	20.7
49V	1535	1760	1810	0.8	9.20	20.8
103V§	1420	1480	1600			
50V	1435	1555	1690	1.7		21.9
51V	1535	1575	1735	2.2	9.03	22.5
52V	1455	1575	1685	1.9	8.93	22.1
53V	1450	1535	1655	2.1	9.70	17.3
55V	1470	1525	1625	1.5	9.07	20.5
66V	1390	1525	1635	1.7	8.75	23.3
68V	1450	1515	1630	1.8	8.93	21.5
69V	1440	1500	1600	1.1	8.57	24.5
70V	1370	1525	1640	1.8	8.62	25.7
104V§	1300	1470	1545	1.7	7.70	31.5
79V	1410	1470	1605	2.4	8.56	25.3
81V	1440	1500	1615	1.4	8.66	23.0
83V	1370	1510	1640	1.6	8.62	24.0
105V	1435	1530	1640	1.9	8.20	23.9
106V§	1330	1470	1560	1.7	8.0	31.5
107V	1450	1510	1630	1.8	8.45	23.1
108V§	1355	1415	1540	1.9	7.45	32.4
109V	1425	1515	1645	2.1	9.25	13.05
101V	1405	1490	1600	1.9	7.00	35.0
110V	1385	1465	1550	1.8	7.40	33.4
96V	1480	1575	1670	1.5	7.37	33.2
95V	1440	1540	1660	2.3	8.1	24.9
97V	1500	1620	1725	2.2	7.85	28.4
98V	1485	1545	1675	2.1	7.8	27.5
111V	1470	1540	1635	1.8	8.44	19.8
112V	1450	1570	1680	1.6	7.90	33.5
99V	1465	1565	1665	1.3	8.16	23.1
113V	1535	1600	1725		7.70	28.2
114V	1515	1585	1700	1.8	7.62	30.1
115V	1395	1500	1620	2.1	7.55	31.0

* Commercial India kyanite brick (5 samples).
† South Carolina topaz brick from commercial manufacturers (5 samples).
‡ Two determinations only.
§ Same composition as preceding brick but hand pressed.

cast mullite-corundum and corundum, and diaspore are included for comparison as well as commercial India kyanite brick. The load-test curves for these are shown in Fig. 5.

XVII. Constant-Temperature Load Test

The A. S. T. M. firing schedule for super-refractories is shown in Fig. 6. Inasmuch as the standard maximum temperature of 1450°C. was not high enough to

TABLE XI

CONSTANT TEMPERATURE LOAD-TEST RESULTS

Brick description	Deformation (% at 1550°C., 25 lb./in.²)
India kyanite	
Average of 7 commercial samples	3.06
High	4.55
Low	1.10
South Carolina topaz	
Average of 2 commercial brick	1.65
Average of 3 brick (BM 34C, 35C, 36C)	2.00*
Bonded electric-furnace mullite-corundum	
Average of 5 samples (BM 63C, 56C, 57C, 58C, 59C)	1.04*
High	1.3
Low	0.8
BM 60C	1.1
Electric-furnace mullite-corundum and topaz	
PM 71C	1.1
Electric-furnace mullite-corundum and domestic kyanite	
BM 87C	1.1
Electric-furnace mullite-corundum, kyanite, and topaz	
BM 116C	1.0
Calcined domestic kyanite and raw topaz	
BM 102C	0.0

* BM Nos. 34C, 35C, 36C, and 63C were preheated in a laboratory test kiln to 1500°C. and fired in a commercial kiln to cone 20.

evaluate the deformation under load of India kyanite refractories, the temperature was raised to 1550°C., as shown in Fig. 6. The load for this test (C) was held also at the standard 25 lb. per sq. in.

(1) Results of Load Tests

The compositions of the brick made by the Bureau of Mines that appeared to be as good as or better than the average of commercial India kyanite brick are given in Table VIII. For comparison, some of the hand-pressed brick that were identical in composition to the dry-pressed brick were included although they were inferior to the dry-pressed specimens. The load-test data for these brick, as well as data for the India kyanite and experimental topaz made by refractory manufacturers, are given in Tables X and XI. Load-test curves for representative samples of these are shown in Fig. 7. The prefix BM refers to brick made by the Bureau of Mines. The suffix V refers to the variable-temperature, and the suffix C refers to the constant-temperature load test.

XVIII. Summary of Results

(1) India Kyanite

Considerable variation was found among the commercial brick supplied by the manufacturers. The average weight of standard-size brick in general is high and the porosity low. The characteristics of the brick depend to a large extent on the quality of the India kyanite used. All of the brick, however, were

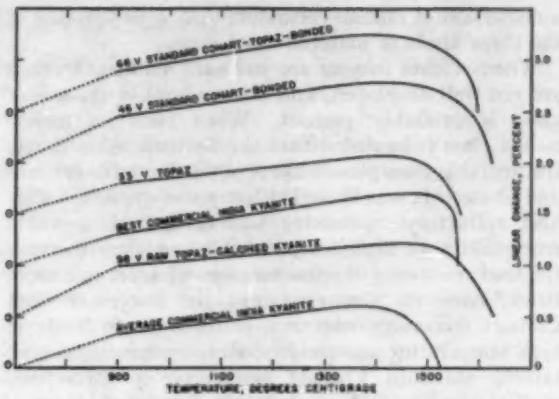

FIG. 7.—Variable temperature load tests on experimental refractories and commercial India kyanite.

superior in load resistance to the diaspore and flint-fire-clay brick.

(2) Topaz

The load resistance of the topaz brick at high temperatures was similar to that of India kyanite refractories. The porosity of the fired topaz brick was higher than that of brick made from India kyanite. The weight of standard size brick was lower.

Brick specimens BM Nos. 28V, 29V, and 30V were made from South Carolina topaz calcined by the Carborundum Co. These brick were preheated at 1650°, 1700°, and 1750°C., respectively, and their load resistance at elevated temperatures was determined. The load resistance increased with the temperatures of preheat, but these temperatures are above those used in commercial firing. A petrographic examination of BM Nos. 28V, 29V, and 30V showed that the sizes of mullite crystals increased with the severity of the heat-treatment.

Brick BM Nos. 31V and 32V were made from topaz calcined at Wilson Dam at 1425° and 1590°C., respectively. This difference in temperature of calcination had little effect on load resistance of the brick.

(3) Andalusite

Brick BM No. 37V was made from rock taken from the New Camp deposit in California, which is owned by the Champion Spark Plug Co. and operated by Champion Sillimanite, Inc. The variable temperature (V) load test indicates that high-grade refractories can be made from this material.

(4) Bonded Electric-Furnace Mullite-Corundum

These bonded refractories had the greatest load resistance of any of the experimental brick tested except possibly BM No. 102C, which was composed of raw topaz, calcined kyanite, and kaolin. The porosity was low as a result of the nonporous character of the electric-furnace mullite-corundum grog. Because of the specific gravity of the grog (about 2.96), the weight of standard-size brick was high. Part I gives

a discussion of mullite-corundum and a description of the three kinds of material used here.

When silicate fusions are suddenly chilled, crystals are not well developed, and a considerable amount of glass is probably present. When such an undercooled glass is heated within the devitrification range, the unstable glass phase changes into the stable crystalline phase. It was thought that water-quenched Corhart refractory containing undercooled glass would recrystallize at high temperatures and thus increase the load resistance of refractories in which it was used. Brick, however, that contained the water-quenched Corhart refractory were not so resistant to loads at high temperatures as corresponding compositions containing standard Corhart refractory or corundum-mullite (pig No. 2014) made by the Bureau of Mines.

Because of the rapid cooling, the water-quenched Corhart refractory was friable and contained blebs. The bulk specific gravity of water-quenched Corhart grog was 2.84, which increased to 2.95 when the grog was heated to 1700°C. Standard Corhart grog had a bulk specific gravity of 2.96 and remained unchanged when the grog was heated to 1700°C. On account of specific-gravity changes, the water-quenched grog decreased in volume in firing whereas standard Corhart grog was volume-constant. This indicates the probable reason for the failure of the brick made from water-quenched grog to withstand as high a load test as those containing standard Corhart grog.

(5) Electric-Furnace Mullite-Corundum and Topaz

As would be expected, the addition of calcined topaz to mullite-corundum lowered the weight and increased the porosity of standard-size brick. The load resistance at elevated temperatures was somewhat inferior to bonded mullite-corundum, but the average was about the same as that of India kyanite refractories. The porosity was also similar. They should withstand thermal shock better than the mullite-corundum refractories, but they are probably inferior to India kyanite in this respect.

The high-temperature load resistance of water-quenched mullite-corundum and topaz combinations was inferior to those that contained slowly cooled, well-crystallized mullite-corundum and, except for No. 69V, were inferior to the average of commercial India kyanite brick.

(6) Mullite-Corundum and Domestic Kyanite

The characteristics of refractories of this class were similar to those of electric-furnace mullite-corundum and topaz composition. The best of these were not so good as the best of the India kyanite brick. To obtain satisfactory load resistance with combinations of mullite-corundum and domestic kyanite, it was necessary to precalcine the kyanite to secure thorough expansion of the mineral before it was incorporated in a refractory batch. Raw kyanite expanded and produced a poor structure.

(7) Domestic Kyanite

A fairly satisfactory brick was processed by first making a grog consisting of 90% of Celo kyanite (already calcined at 1500°C.) and 10% of Edgar plastic kaolin and firing to 1500°C. The grog was then crushed, bonded with 10% of Edgar plastic kaolin, and refired at 1500°C. The brick did not expand in the refiring. The load resistance at high temperatures was fair. The porosity, however, was very high (35%), and standard-size brick weighed only 7 lb. A brick slightly inferior to the foregoing sample, with 90% of calcined Virginia kyanite bonded with Edgar plastic kaolin, showed only a slight expansion in the preheat, and it was unnecessary to crush and rebond it. The substitution of 10% of raw topaz for an equivalent amount of kyanite greatly improved the load resistance at high temperatures.

(8) South Carolina Topaz and Domestic Kyanite

This combination offers some interesting possibilities inasmuch as raw topaz on firing forms an excellent bond either with raw or calcined kyanite. The results indicate that a minimum of 22½% of raw kyanite may be incorporated in the composition when 45% of raw topaz is used. Only 1% of linear expansion occurred into the preliminary firing before the load test. With 45% of raw topaz and of raw kyanite, an excellent bond was obtained, but blisters appeared on the brick surfaces after firing. The best specimen of this class tested was BM 109V, which contained 60% of calcined Celo kyanite with 30% of raw topaz and 10% of Edgar plastic kaolin. The load resistance of these at elevated temperatures compared favorably with the best of the bonded electric-furnace mullite-corundum refractories and were superior to commercial India kyanite brick. Specimen BM 111V, which contained calcined Georgia kyanite, had a porosity of less than 20%, which was as low as that of any India kyanite refractories. No clay is necessary in these brick; specimen BM 96V (containing 50% each of raw topaz and calcined kyanite) was well bonded and showed excellent results in the load tests.

The reasons for the peculiar bonding properties of raw topaz are not thoroughly understood. There is valid evidence, however, that part of the decomposition products of the topaz are retained by the kyanite.

If factory conditions are such that the fumes given off by the topaz during firing do not create a health hazard, the cost of precalcining the topaz may be eliminated. The cost of these raw materials should be less than $100 per thousand f.o.b. mines, as compared with about $225 per thousand for calcined India kyanite.

Acknowledgment

The writers wish to acknowledge the assistance given by D. F. Allen in processing refractories and collecting load-test data. The following corporations, moreover, furnished materials and information that made this study possible: Kyanite Products Corp., Yancey County Cyanite Co., United Feldspar and Minerals Corp., A. P. Green Fire Brick Co., Champion Spark Plug Co., Corhart Refractories Co., The Carborundum Co., The Charles Taylor Sons Co., Harbison-Walker Refractories Co., Mullite Refractories Co., General Refractories Co., Laclede-Christy Clay Products Co., The Vitrefrax Corp., and Battelle Memorial Institute.

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STUDY OF DIFFUSION IN GLASS*

By J. A. Pask and C. W. Parmelee

Abstract

An introductory study was made of diffusion into glass from salts, with silver nitrate as the chief source of diffusing particles. The optimum test conditions were a temperature of 900°C. and a test time of 108 hours. The results noted were (1) effect of time, (2) effect of temperature on the distance of diffusion, (3) variation of silver concentrations in the glass with the distance of diffusion, and (4) a check of Fick's law of diffusion. The concentration gradient of silver from a diffusing interface was determined with the use of a spectrograph and corresponding particle sizes with an ultramicroscope. In addition to the silver nitrate, a number of other salts were tested at several temperatures. The development of Liesegang rings was noted in some of the samples. The nature of diffusion in glass was deduced from the results.

I. Introduction

The role of diffusion in ceramic processes is of first-rate importance. A few examples that may be cited are (1) the diffusion of iron oxide from the hot end to the cold end of silica brick set in the crown of an open-hearth furnace; (2) the diffusion of the components of slags and other vitreous fusions in contact with refractories at high temperatures; (3) the growth of crystals in fired clays, ceramic bodies, and glasses; and (4) the diffusion of color oxides and compounds in bodies, stains, and glazes. The significance of diffusion in solid state reactions should also be mentioned.

The possible application of such studies to new methods of decoration is of still greater practical importance, especially when discoloration sets in with the migration of the substance into the glass surface.

The research reported in this paper is of an exploratory nature. A series of fundamental experiments was made to study the nature and the rates of diffusion from certain compounds for a number of time and temperature intervals. Diffusion took place from a salt into a commercial flint glass in all cases, that is, in a lime-soda-silica glass. One or more salts of Cu, V, Th, Pb, Au, Cr, Pt, Co, Fe, and Ag were tried. Silver was used, however, for most of the experiments because of its rate of migration and its pronounced tendency for coloration, which allow the use of relatively simple methods for measurement of the diffusion.

II. Review of Literature

The literature on the general subject of diffusion is relatively meager.

(1) Diffusion Coefficients

Some of the diffusion coefficients as compiled from the literature are given in the opposite column.

(2) Equations Relating to Diffusion

(*A*) *Fick's Law:* Fick's law has long been the fundamental basis for the study of diffusion in liquids on a quantitative basis. The law states specifically that the driving force which impels a dissolved substance to move from a place in a solution of higher concentration to one of lower concentration and which also determines the rapidity of the movement of the particle is proportional to the drop in concentration. A mathematical representation to fit this law is given in equation (1).

$$\frac{dc}{dt} = -qD\frac{dc}{dx} \qquad (1)$$

c = concentration
t = time
q = cross section (sq. cm.)
x = distance of point in interior of sample from surface
D = diffusion coefficient, i.e., expression representing area required to permit diffusion of unit volume (or mass) in unit of time at temperature, t°C.

With the assumption that D is independent of the concentration and is a constant, the general form of the diffusion equation (2) is obtained.

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \qquad (2)$$

This equation represents diffusion only in the x direction. Jost[1] discusses cases and presents equations to cover any concentration distribution.

The form given in equation (2) is not valid for all cases for it has shown a small deviation from the experimental results because of the assumption that D is a constant. D, moreover, has been found actually to be a constant only for nonelectrolytes at low concentrations, for some solid substance, and in silicate melts for small masses of dissolved substances; otherwise it

Compilation of Diffusion Coefficients

	Cm.²/day
Most salts in aqueous solutions	0.26
Common salt in water at 15°C.	1.00
Aqueous NH_3SO_4 in water at 8°C.	1.01
Diopside in liquid mixture at 1500°C.	0.14–0.2
Molten metals in other molten metals	2.59
Gold in molten lead at 492°C.	3.00
Solid gold in solid lead at 150°C.	4.3×10^{-8}
Silver into glass at 354°C.	2.2×10^{-6}

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 22, 1942 (Glass Division). Received September 1, 1942.

Based on a thesis submitted by the senior author in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Illinois, Urbana, Ill., October, 1941.

[1] Wilhelm Jost, Diffusion and Chemical Reactions in the Solid State. Theodor Steinkopff, Leipzig, 1937; *Ceram. Abs.*, **17** [8] 292 (1938).

changes with concentration. A solution of the equation with a variable D, however, would be most difficult to obtain and would have to be integrated by a process of Boltzmann, whereas with a constant D, a simple integral can be stated. The fact must also be considered that Fick's equation is valid only for a single homogeneous phase; with polyphase systems, a corresponding equation would have to be established for each phase. A consideration of the interfaces in a polyphase system would also have to be taken into account.

(*B*) *Solving for D from Fick's Law:* Integration of Fick's equation according to Stefan[2] and also by Warburg[3] gives equation (3).

$$D = \left(\frac{M}{\sqrt{t}}\right)^2 \cdot \frac{\pi}{4N^2} \qquad (3)$$

N = saturation concentration per cc.
M = amount of material immigrating per sq. cm.

Inasmuch as D is a constant, equation (4) can be obtained.

$$\frac{M}{\sqrt{t}} = k \qquad (4)$$

(3) Diffusion of Silver in Glass

The first quantitative investigations on the diffusion of silver into glass were conducted in 1913 by Schulze.[4] His work was prompted by that of Heydweiller and Kopfermann,[5] who found that silver introduced from molten silver nitrate is not only readily electrolytic but it also migrates merely by diffusing in the glass and with no difference of electrical potential.

Schulze's results showed that, at a constant temperature, the amount of silver diffusing into the glass is proportional to the square root of the time of diffusion (equation (4)). It was also demonstrated that, within the limits of observational errors, the decrease of concentration of the silver in the glass as it penetrates into the interior of the specimen is directly proportional to the distance and is represented by a straight line. Figure 1 represents this condition.

A series of tests was made by Halberstadt[6] on diffusion of silver in glass at 565° to 615°C. His results were found to agree with equation (4). Halberstadt, however, suggests that silver atoms rather than silver ions diffuse into the glass, and he supports this assumption with the knowledge of an atomic dispersed condition of metals in glass based on the Nernst distribution law. The ratio of concentration of Au in Ag to Au in glass, for example, was found to be a constant; therefore, because gold dissolves monatomically in silver, it must also be atomically dispersed in glass.

Kubaschewski sought to prove that silver diffused

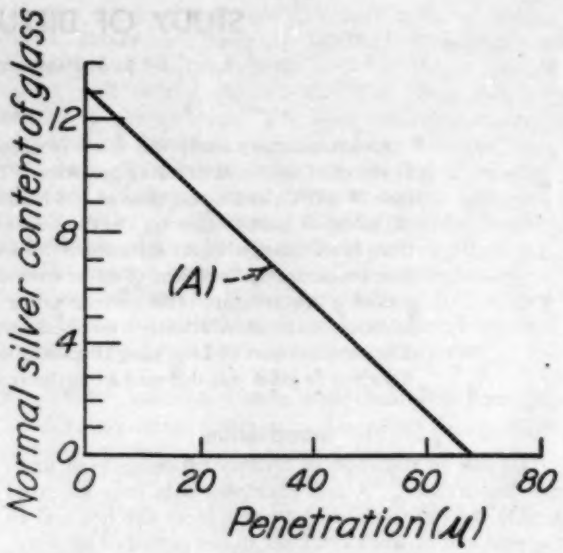

FIG. 1.—Relation of silver content of glass to depth of penetration (according to Schulze[4]); curve *A*, immersed 12 hr. at 354°C. in pure $AgNO_3$.

into glass as ions assisted by the formation of an intermediate oxide[7]. If atoms diffuse into the glass, the process then must be independent of the oxygen pressure of the surroundings. The suggested mechanism of reaction, however, which assumes that primary Ag_2O forms on the surface of the glass and that after its decomposition silver ions diffuse into the glass while the sodium ions function as oxygen-acceptors, would depend on oxygen pressure. The validity of this reasoning was substantiated by the actual experimental results. Below an oxygen pressure equivalent to 40 mm. of Hg, the diffusion was strongly dependent on the oxygen content.

Alexander[8] has mentioned the work of R. Zsigmondy on silver glasses. Zsigmondy's experiments showed that silver goes into solution in the glass first as oxide, then it is reduced to the metal, and finally it is found in the chilled glass as a colloidal dispersion.

Summarizing, equation (4) has been shown to hold experimentally in all cases. Three possible theories were reported for diffusion of silver into glass, namely, as ions, as atoms or aggregated particles, and as the oxide.

Table I is a compilation of the diffusion coefficients as determined by the workers cited. Although the values indicate the trend and magnitudes, they are not directly comparable inasmuch as these investigators used glasses of different compositions. This fact and the probability that the softening temperature lies between 540°C. and 565°C. account for the observed rapid rise of coefficients between these two temperatures.

[2] I. Stefan, *Wiener Sitzungsberichte*, **79**, II, 161 (1879).
[3] E. von Warburg, "Diffusion of Metal in Glass," *Ann. Physik*, **40**, 327–34 (1913).
[4] Gunther Schulze, "Experiments Concerning Diffusion of Silver in Glass," *ibid.*, **40**, 335–67 (1913).
[5] A. Heydweiller and F. Kopfermann, "Knowledge of Electrolysis of Glass," *ibid.*, **32**, 739–48 (1910).
[6] Joseph Halberstadt, "Diffusion of Silver and Copper in Glass," *Z. Anorg. Allgem. Chem.*, **211** [1–2] 185–94 (1933); *Ceram. Abs.*, **13** [3] 56–57 (1934).
[7] O. von Kubaschewski, "Diffusion of Silver into Glass," *Z. Elektrochem.*, **42** [1] 5–7 (1936); *Ceram. Abs.*, **17** [3] 99 (1938).
[8] Jerome Alexander, Colloid Chemistry, Theoretical and Applied, Vol. II. Chemical Catalog Co., New York, 1932. 734 pp.; *Ceram. Abs.*, **11** [10] 543 (1932).

TABLE I

DIFFUSION COEFFICIENTS OF AG INTO GLASS

Temp., °C.	D (cm.²/day)	Author
354	0.22×10^{-4}	Schulze[4]
540	0.95×10^{-4}	Kubaschewski[7]
565	9.85×10^{-4}	Halberstadt[6]
590	11.32×10^{-4}	"
615	13.65×10^{-4}	"

(4) Other Diffusion Experiments

Other studies on diffusion in silicate melts are those of Endell[9] and Bowen[10]. Endell demonstrated the interdiffusion of lime and microcline glasses. Bowen made quantitative experiments on the diffusion of diopside, a heavy liquid, into a plagioclase, a light liquid, above the fusion point of both at about 1500°C.

Wessels[11] studied the thermolytic concentration changes in glass in relation to the Ludwig-Soret effect, which refers to the movement of material from the hot end to the cold end of a substance.

Fettke and Stewart[12] discussed the rates of diffusion and of solution with respect to attack of refractories by slag. They used equation (5) to express this relation, which is another form of Fick's law.

$$\frac{dc}{dt} = Dq(S_{sat.} - S_{act.}) \qquad (5)$$

$S_{sat.}$ = amount of diffusion substance that glass can hold.
$S_{act.}$ = amount of diffusing substance already present in the glass.

Equation (5) is identical in form with that of a unimolecular reaction, assuming that the rate of diffusion determines the total reaction rate. Actual tests indicate that the diffusion of the solution materials from the interface is not the controlling factor in the slagging action of coal ash on aluminous silicate refractories.

Gilard and Dubrul[13] attempted to determine some of the controlling factors on the degree of coloration with silver and copper staining, as a practical application of thermal diffusion. Their method was to note the effect of small concentrations of different materials on the intensity of transmitted light through the sample.

Halberstadt[6] measured the diffusion velocity of copper into glass and found D_{Cu} to be 1.79×10^{-4} sq. cm. per day at 650°C. as compared with D_{Ag} of 13.65×10^{-4} sq. cm. per day at 615°C.

III. Experimental Procedure

(1) Glass Samples and Tests

The glass samples were prepared in the form of small cups with thick walls that also acted as the containers for the diffusing material. With the use of fused alumina crucibles, into which the glass cups fit snugly and which offered them some physical support, test temperatures up to 900°C. could be maintained at constancy with proper potentiometer control for as long as 108 hours.

A commercial flint glass was used, which had the following chemical composition:

	Batch calculation (%)	By analysis (%)
SiO_2	74.5	74.80
Na_2O	16.5	15.70
CaO	4.0	3.98
MgO	2.8	3.04
Al_2O_3	0.5	1.02*
B_2O_3	0.5	0.47
BaO	0.5	0.26
		99.27

*$Al_2O_3 + Fe_2O_3$.

An interferometer expansion test showed that the softening point was 565°C., and the thermal expansion coefficient from room temperature to 500°C. was 9.9×10^{-6} cm. per cm. per °C. Inasmuch as silver was found to diffuse the most readily, the major portion of the experiments was performed with silver salts. Those used were $AgNO_3$, AgCl, Ag_2SO_4, and Ag_2O. Silver nitrate was also heated up to 700°C. in test tubes of Pyrex-brand and Corning D172 glasses.

(2) Measurements

(*A*) *Increase of Weight:* The amount of material diffusing into the glass cups was determined by weighings, and the following weights were obtained for the calculations: Weight of (*a*) the glass cup, (*b*) the cup plus salt, and (*c*) the cup plus the diffused material. The difference between (*b*) and (*a*) was the weight of the salt used. In order to eliminate as many variables as possible, this weight always corresponded to 0.0043 gm. equivalent of salt. This amount in most cases filled about half the well.

After the experiment, the residue in the well was dissolved with a suitable acid, the sample cup was washed and dried, and the third weight (*c*) was obtained. The difference between (*c*) and (*a*) was the increase in weight caused by the material diffused into the glass. This weight was not the true weight, however, because there was a simultaneous diffusion of sodium from the glass into the salt. This exchange was verified by the works of Schulze[4] and Kubaschewski.[7] The true weight of the silver diffused into the glass may therefore be calculated according to equation (6).

$$M - M\frac{Na}{Ag} = G \qquad (6)$$

M = amount of silver entering glass.
G = increase of weight of sample cup.
Na and Ag represent corresponding molecular weights.

Equation (6) may also be expressed as the weight of incoming silver minus an equivalent weight of outgoing sodium, which is equal to the actual increase of weight. By substituting known values, $M = 1.272G$, which

[9] Kurd Endell, "Diffusion Phenomena in Silicate Fusions at High Temperatures," *Neues Jahrb. Mineral., Geol.*, **2**, 129–54 (1913).

[10] N. L. Bowen, "Diffusion in Silicate Melts," *Jour. Geol.*, **29** [4] 295–317 (1921); *Ceram. Abs.*, **1** [1] 8 (1922).

[11] Herman Wessels, "Thermolysis; Ludwig-Soret Phenomena in Solid States," *Z. Phys. Chem.*, **87**, 246 ff. (1914).

[12] C. R. Fettke and W. E. Stewart, "Slagging Action of Western Pennsylvania Coals on Different Types of Refractories in Small Pulverized Coal Installation," *Carnegie Inst. Tech., Mining & Met. Invest., Coop. Bull.*, No. 73, 90 pp., (1936); *Ceram. Abs.*, **17** [1] 24 (1938).

[13] P. Gilard and L. Dubrul, "Coloration of Glass by Staining, III," *Jour. Soc. Glass Tech.*, **20** [80] 225–44 (1936); *Ceram. Abs.*, **17** [1] 11 (1938).

gives the weight of silver diffused into the test glass sample. These values are recalculated on the basis of grams per unit area of diffusion interface and the average number of grams per unit volume of diffusion.

(*B*) *Extent of Diffusion:* The sample cups were weighed, cut in half vertically with a diamond wheel, ground, and polished. The polished cut faces of the sample cups to be used for quantitative measurements and those showing unusual and significant effects were photographed with a Micro-Tessar IIb lens at a magnification of 5×. The necessary measurements were then made from the photographs.

In order to compensate for the possibility of a non-center slice through the sample and thus for the measurement of an incorrect diameter on the photograph, the method for determining the true diameter was derived (see Fig. 2). Micrometer calipers were used to measure the "radius" of the well. The correction ratio of 1.4 over *A* obtained from Fig. 2 applied to all linear and areal measurements on the particular photograph.

An application of a modified Simpson's rule or a graphical and arithmetical integration was used to obtain the area of the diffusion interface and the diffusion volume from these photographs. This method was necessary inasmuch as the vertical cross section of the bottom of the well did not correspond to the trace of any of the simple curves, such as a circle, parabola, or ellipse.

The procedure consisted first of lining out horizontal strips on the photographs, a greater number being present in the portion of greater curvature. The average length of each strip was calculated, and a correction was made, using the ratio obtained from Fig. 2. The surface area of diffusion for each strip was then calculated from the formula, namely, area of cylindrical strip equals $\pi d_{avg.}$ times height or thickness of strip, because a horizontal cut through the sample shows a circular trace. The total area would thus be the arithmetical summation of the strips as shown in equation (7).

$$A = \sum \pi d_{avg.} \times h \qquad (7)$$

The volume of diffusion may also be calculated with the aid of these strips. The average length of the strip, however, including the extent of the diffusion, d_2, is obtained in addition to the length of the well itself, d_1. Equation (8) is thus evolved.

$$V = \sum \frac{\pi}{4} h(d_2^2 - d_1^2) \qquad (8)$$

In cases where the salt had flowed over the edges of the well, the increased area and volume of diffusion were calculated with the use of the proper geometric formulas for circles and cylinders.

Dividing the volume by the area for a given sample gives the distance of diffusion. This value corresponds within experimental error with the actual measured distance from the photographs.

(*C*) *Observation of Colors:* In all of the tests, the color of the diffused portion of the sample was noted as well as its change and appearance for different temperatures and times. The samples were also exposed to ultraviolet light with a wave length of 3650 a.u., and the presence and type of fluorescence were observed.

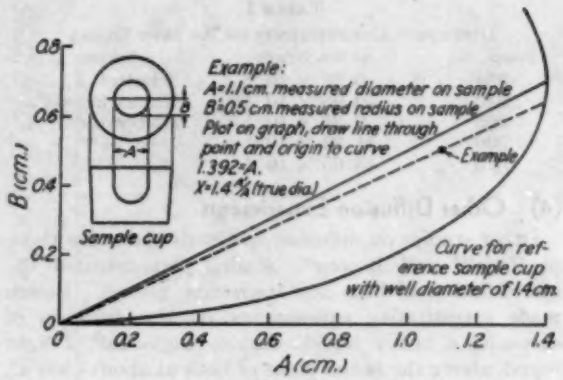

FIG. 2.—Method of correcting for true diameter of diffusion well in test sample.

(*D*) *X Rays:* In order to determine the nature of the colloidal particles, Laue X-ray patterns were obtained of several samples into which diffusion from $AgNO_3$ had taken place. A thin wedge of the glass was ground for this purpose.

(*E*) *Ultramicroscope:* A slit ultramicroscope was used to observe a glass sample into which diffusion from $AgNO_3$ had been maintained for 36 hours at 900°C. Two surfaces were ground at right angles and highly polished, and this sample was used in the setup in place of the ordinary cell. A thin section of the same sample was also made by petrographic methods and examined with a cardioid ultramicroscope.

(*F*) *Spectrograph:* An approximate quantitative concentration gradient was determined for the same sample with a Bausch & Lomb medium quartz spectrograph, using spark excitation. This method offers excellent opportunities for further work.

A working or calibration curve was first obtained by making a series of glasses of known silver concentrations, with AgCl as the source of silver. Silicon was used as the internal standard because of its comparatively high concentration in relation to the silver content. The intensities of each one of the silver and silicon lines were measured with a microphotometer, and their ratios were then plotted against silver concentration. For the determination of an unknown quantity, the ratio of the intensities of the same two lines was located on the calibration curve and the silver percentage was read off.

IV. Results

(1) Diffusion from $AgNO_3$ as a Source

Of the silver salts, $AgNO_3$ was used the most extensively, and the most complete results were thereby obtained.

Silver nitrate melts at 212°C. and decomposes at 444°C., which is above the decomposition temperature at 300°C. for Ag_2O, to form metallic silver. This decomposition is rapid, which causes some of the contents

to boil over the edge of the well and thus form a larger area and volume of diffusion. Above the decomposition temperature, the source of silver is no longer $AgNO_3$ but metallic silver, which is in very close contact with the glass.

All of the tests were performed under nonrestricted diffusion because the samples were thick enough that the diffusing material at no time reached the outer edges of the cup.

(*A*) *General Appearance:* Examination of Table II shows that color variation depends mainly on the temperature and that extended time has little effect. Below the softening point of the glass, the diffusion color is a dark reddish brown. Bands of different shades of color and translucency are formed above the softening point in addition to the brown, which is the farthest from the source of diffusion.

With ultraviolet light, however, both temperature and time are important; for instance, with samples exposed to diffusion for 108 hours, the brightest fluorescence was present at 400°C. The fluorescence at 500°C., however, was good for short test-time intervals but began to fade in pieces held for 108 hours. Fluorescence at higher temperatures was present only in some of the rings.

After the residue had been dissolved, it was apparent that some reaction had occurred between the salt and the glass surface inasmuch as the surface was rough and pitted.

There was no appearance of diffusion or reaction when $AgNO_3$ was tried in a tube made of Corning D172 glass up to 700°C. With Pyrex-brand glass tubes, a lighter brown color and a smaller distance of diffusion were noted with presence of some reaction.

(*B*) *Effect of Time on Distance of Diffusion:* The time-distance diffusion curves for $AgNO_3$ at 500°C. and 900°C. are shown in Fig. 3, plotted from data given in Table II. The curves do not start at zero because the samples were heated with the furnace and some diffusion had occurred before the constant test temperature was reached.

The time rate of diffusion is not constant for extended times. It is rapid and close to constancy in the early stages, followed by a decrease.

The photographs in Fig. 4 show the actual appearance of the samples at 500°C. for various test-time intervals.

(*C*) *Effect of Temperature on Distance of Diffusion:* Figure 5 illustrates the temperature-distance diffusion curves for $AgNO_3$ at 12 hours and at 108 hours. Both approach the temperature axis asymptotically and do not have a constant temperature rate.

For 12 hours of test time, a rapid increase occurs in distance of diffusion at about 700°C. because less resistance is offered to the passage of silver particles. At temperatures above the softening point, a large number of bonds in the glass structure are broken, resulting in larger holes. The curve flattens out at 900°C., but it probably would increase rapidly at about 1100°C. because of accelerated decrease of viscosity of the glass.

For 108 hours at 200°C., there was no measurable distance of diffusion, but a surface discoloration was present. A comparatively rapid increase in diffusion occurs at about 500°C., which may be the result of the decomposition of the nitrate.

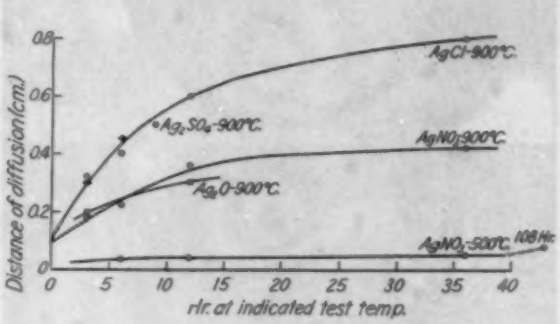

FIG. 3.—Effect of time on distance of diffusion from some salts at a given temperature.

TABLE II

DIFFUSION DATA IN RELATION TO $AgNO_3$

Temp., °C.	Time* (hr.)	Diffusion: Area (cm.²)	Diffusion: Volume (cm.³)	Diffusion: Distance (cm.)	Increase wt./area (gm./cm.²)	Increase wt./vol. (gm./cm.³)	Color	Fluorescence
200	108	None	None	None	None	None	Faint brown	Very faint yellow
300	108	3.87	0.031	0.008	0.0081	1.014	Reddish brown	Yellowish brown
400	108	3.16	0.129	.036	.0031	0.811	" "	Bright yellow
500	108	10.00	0.768	.080	.0058	.076	" "	Faint light brown
500	36	7.86	0.390	.050	.0069	.139	" "	Yellow
500	12	8.46	0.350	.040	.0096	.231	" "	"
500	6	6.28	0.204	.034	.0097	.298	" "	"
500R†	12	5.30	0.133	.026	.0049	.193	" "	"
600	12	9.56	0.699	.076	.0053	.072	Brown	Very faint brown
700	12	8.74	1.850	.190	.0133	.063	Dark brown, light band on edge	None
900	36	8.53	3.477	.440	.0421	.103	Bands of different colors: yellowish-white, clear gray, brownish-yellow, reddish-brown, brown, and yellow rings	Yellow colors give yellowish-white fluorescence; reddish brown give yellow
900	12	7.76	2.960	.340	.0390	.102		
900	6	7.63	1.922	.220	.0308	.122		
900	3	7.57	1.550	.180	.0242	.118		
900	0	8.55	0.858	.100	.0136	.135		
1100	6							Yellowish around edges

* All of the time values listed indicate the time of test after the test temperature had been reached.
† Reducing conditions.

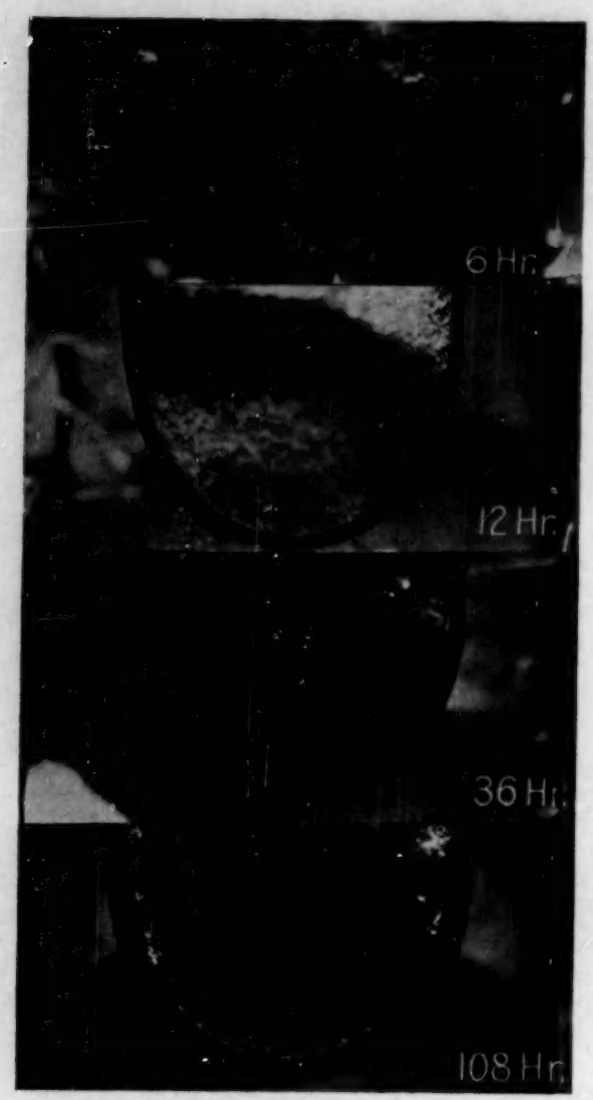

FIG. 4.—Amount of diffusion with varying time at 500°C. using $AgNO_3$ at the start of the test.

At temperatures up to 900°C., convection currents, which are the most difficult factor to cope with in diffusion experiments with aqueous solutions, offer no difficulty inasmuch as the viscosity of the glass is sufficiently high. Above this temperature, however, convection currents were present and interfered slightly with measurements of diffusion.

(*D*) *Variation of Concentration with Diffusion:* The relation of the average silver concentration in the diffused portion of the glass at 500°C., and 900°C. to the time of test is shown in Fig. 6. The curve for 500°C. indicates that the concentration in the diffused glass is highest adjoining the surface. The surface concentration may be assumed to remain about constant, which may be explained by the fact[14] that the

[14] Sophia Berkmann and Gustav Egloff, Emulsions and Foams, p. 3. Reinhold Publishing Corp., New York, 1941.

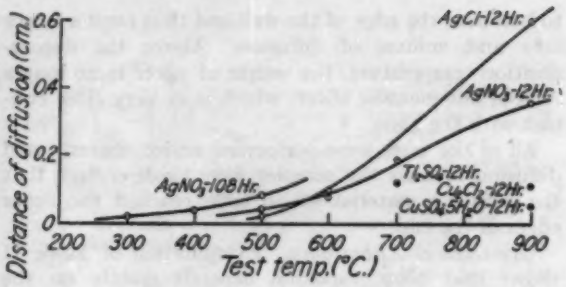

FIG. 5.—Effect of temperature on distance of diffusion from some salts at a given time interval.

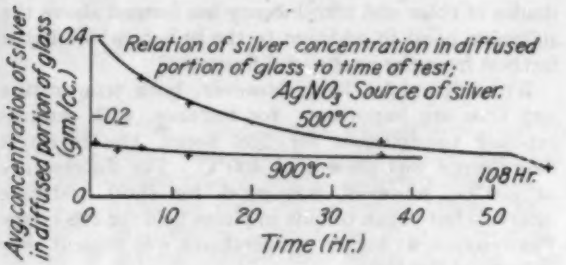

FIG. 6.—Relation of silver concentration in diffused portion of glass to time of test; $AgNO_3$, source of silver.

average concentration will drop because, with increase in time, the migration of ions in the glass is slower than that of new silver ions into the glass surface. As the time and the distance of diffusion increase with unrestricted diffusion, concentration decreases. The migration of silver in the glass at 900°C., however, is practically as rapid as the migration of particles into the glass. The average concentration will therefore remain about constant and lower in value than the 500°C. samples up to a certain time interval even though the amount of silver diffusing into the glass and the distance of diffusion from the surface are greater.

The extension of curves to zero time theoretically would give the surface concentration of silver at a given temperature if the samples were exposed instantly to diffusion. The samples with the diffusing materials in this case were raised to the test temperature, and time was measured from that point.

Figure 7, however, is a plot of the average concentration in the diffused portion against the distance of diffusion. All of the test points for $AgNO_3$ are located and marked. The curve shows a decided break in slope in the region of the softening point of the glass. It is reasoned that there is a marked difference in the nature of the diffusion on either side of this temperature range. The rapid drop in concentration at the lower temperatures also indicates a noticeable resistance to diffusion on the part of the glass. At higher temperatures, the glass offers relatively little resistance because the concentration is practically constant with increased distance of diffusion. At higher temperatures, where a definite decrease of viscosity would occur, it is logical that the curve might again have a change of slope and

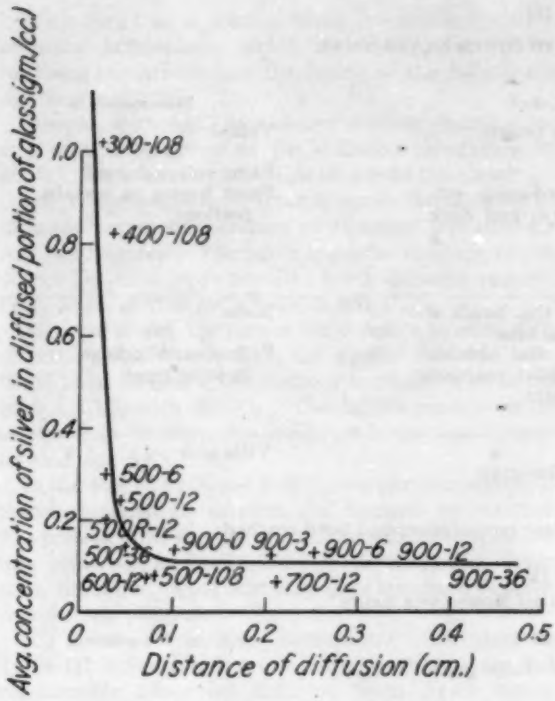

FIG. 7.—Relation of silver concentration in diffused portion of glass to depth of penetration; $AgNO_3$, source of silver. *Note:* 1st number for each point on curve is temperature (°C.); 2d number refers to time of test in hours after reaching test temperature.

start to show an increase in concentration with distance.

(*E*) *Test of Fick's Law:* According to equation (4) if Fick's law with a constant diffusion coefficient applies, *M*, the grams per square centimeter, should be proportional to the square root of time and a straight line should be obtained graphically. Figure 8 indicates this relation. A straight line is obtained at 900°C. during the early stages of the experiment; as indicated by the point off the line at 36 hours, however, the so-called diffusion constant changes for longer times. The high resistance of the glass to diffusion at 500°C. is again indicated by the curve in this figure. The slightly negative slope of the curve is doubtful inasmuch as small experimental errors can produce this effect. The indication of a curve with a flat slope is still present, however, and the extent of the straight-line portion is therefore unknown.

(*F*) *Silver Concentration Gradient:* Schulze[4] showed that at about 400°C. a straight-line drop occurred in the concentration of silver from the surface to the interior of the specimen. Above the softening point or specifically at 900°C. in this case, rings of different colors were obtained. The appearances of these rings were as follows:

Area	Appearance
(1)	Clear glass
(2)	Clear amber brown
(3)	Opaque bluish white with transmitted light brown
(4)	Clear gray with yellowish tinge
(5)	Opaque yellowish white

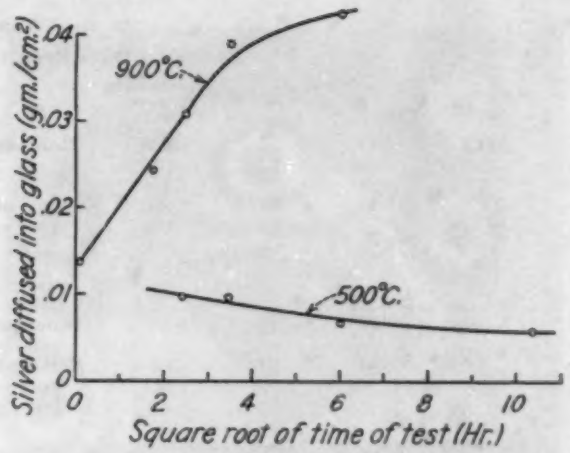

FIG. 8.—Relation of silver diffusing per unit surface to square root of time; $AgNO_3$, source of silver.

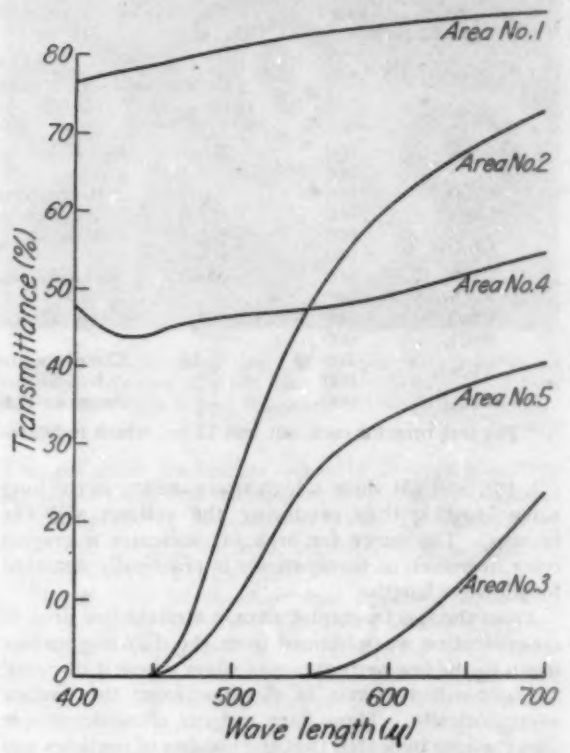

FIG. 9.—Spectrophotometric curves for sample with diffusion of silver from $AgNO_3$ at 900°C. for 36 hr.

Examination with an ultramicroscope revealed that all of the colored areas produced a Tyndall cone, but no continuous change occurred in the number of particles. A relative approximation of particles per unit microscopic area showed none in area (1); particles too concentrated to make a count in area (2); about 475 in area (3); about 6 in area (4); and about 1300 in area (5).

A graphical analysis of the colors of the areas is shown by spectrophotometric curves in Fig. 9. Areas

TABLE III

DIFFUSION DATA RELATING TO OTHER SILVER SALTS

Salt	Temp., °C.	Time (hr).*	Distance of diffusion (cm.)	Color	Fluorescence
AgCl	500	12	0.020	Clear amber brown	Yellow
	500R†	12	.015	" " "	"
	600	12	.10	" " "	Faint yellow-brown
	900	36	.80	Rings of brownish yellow, yellow, and dark gray	Faint brown in certain portions
		12	.60		
		6	.40		
		3	.32		
		0	.11		
Ag_2SO_4	700	12	.30	Brown with thin bands of yellow and blue	None
	900	12	.60	Yellowish, also bluish gray, cellular reaction layer present	Yellow and orange in some rings
		9	.50		
		6	.45		
		3	.30		
Ag_2O	900	12	.30	Yellowish	Yellowish
		3	.20	Yellowish blue-gray	"
	900R†	3	.12	Yellowish	"

* All time values listed indicate the time of test after the test temperature had been reached.
† Reducing conditions.

TABLE IV

DIFFUSION DATA RELATING TO NONSILVER SALTS*

Salt	Temp., °C.	Distance of diffusion (cm.)	Color	Fluorescence
$AuCl_3$	600	None	Salt reduced to metallic gold	
	900	"		
Co_3O_4	900	"	Salt unaltered	
$CuSO_4$	900	0.05	Blue, slight reaction	Yellowish around center
Cu_2Cl_2	600	None	Blue surface; vesicles present	None
	900	0.11		Bluish and yellow
$CrCl_3$	900	None	Surface discolored	
$FeCl_3$	900	"	" "	
$PbCl_2$	700	"	Glass attacked along melt line	None
$PtCl_4$	600	"		
Tl_2SO_4	700	0.12	Colorless, but diffused portion has different index of refraction	Faint yellow
	900	?		Yellow
V_2O_5	900	?	Same as Tl_2SO_4	Yellow on surface

* The test time for each salt was 12 hr., which indicates time of test after test temperature had been reached.

(2), (3), and (5) show a high transparency in the long wave lengths, thus producing the yellows and the browns. The curve for area (4) indicates a grayish color inasmuch as transparency is practically constant for all wave lengths.

From the spectrographic data, a straight-line drop in concentration was obtained from the diffusing surface down to the low percentages of silver where it deviated to approach the axis of distance from the surface asymptotically. These data and the ultramicroscopic observations indicated that the number of particles was not a criterion of concentration and that the sizes of the particles must vary considerably. These data agree with the theory presented by Warburg[3] but they varied slightly from Schulze's[4] experimental results.

X-ray photographic exposures of the brownish and yellowish-white areas showed the presence of very faint lines corresponding to those for metallic silver.

(G) Diffusion Constant: The diffusion constant as calculated from equation (3) cannot be obtained because N_s, the silver saturation value, was not determined. From the data available in Fig. 8, however, it is indicated that D would be a constant only in the comparatively early stages of diffusion because the curves are not straight lines for the entire test-time interval.

(2) Diffusion from Other Silver Salts as Source

In addition to $AgNO_3$, the other silver salts used for a number of tests were AgCl, Ag_2SO_4, and Ag_2O. The following data are given for these salts:

Salt	Melting point (°C.)	Boiling point (°C.)
AgCl	455	1550
Ag_2SO_4	652	Decomposes
Ag_2O	Decomposition at 300	

(A) General Appearance: Table III lists the colors and the fluorescence of the samples in this group. The colors, in general, are the same as those for $AgNO_3$, which indicates that their physical nature is approximately the same regardless of the manner of migration of the particles.

With Ag_2SO_4 as a source of diffusion, one area shows a marked cellular structure between the normal diffusion and the outline of the original well, which is formed by metallic silver from the decomposition of the sulfate. A reaction or strong effusion of a gas evidently is responsible.

With Ag_2O as a source, blebs are formed with a reducing atmosphere which do not appear under oxidizing conditions, and the extent of the diffusion is not so great.

Samples with AgCl as a source of silver do not show any cellular structure at the diffusion interface. At 500°C., there was no noticeable attack on the glass.

(*B*) *Diffusion Data:* Figure 5 shows the distance of diffusion versus temperature at 12 hours' test time for AgCl as a source. The curve is similar in shape to the others but rises more rapidly, being diffused roughly twice as far as that for $AgNO_3$ at 900°C.

Figure 3 shows the curves for distance against time of test. All of them again are similar in shape. At 900°C. and 36 hours, the distance is about twice as far with AgCl as with $AgNO_3$. The Ag_2SO_4 curve roughly corresponds to that for AgCl, and the Ag_2O curve to that for $AgNO_3$.

In the case of AgCl and Ag_2SO_4, the particles diffusing therefrom must be smaller, and because no reaction was present with the use of AgCl, the diffusing particle was probably a simple ion. With the other silver salts, the diffusing particle may have consisted of some complex ion or atom.

(*C*) *Effect of Reducing Atmospheres:* The data in Table III indicate that a CO reducing atmosphere had considerable effect on diffusion from Ag_2O, which corresponds to Kubaschewski's theory that the role of oxygen is important. The diffusing particle at some stage is possibly a combination of silver and oxygen This theory, however, does not have general application inasmuch as the distance of diffusion from AgCl in both atmospheres is within experimental error.

(3) Diffusion from Nonsilver Salts

Other salts were selected to determine their tendency to diffuse and the resulting colors. The results are given in Table IV. Only the salts of copper, thallium, and vanadium showed any diffusion. The copper formed a blue coloration, and the others were colorless. In all cases of diffusion, fluorescence was also present.

Figure 5 includes the points for those salts that show measurable diffusion. The order of increasing diffusion with the salts as a source is $CuSO_4 \cdot 5H_2O$, Cu_2Cl_2, Tl_2SO_4, $AgNO_3$, and AgCl.

Some type of reaction between the copper salts and the glass occurred because a cellular structure was formed. Thallium sulfate as a source showed a colorless but easily noticeable diffusion because of the large difference in indices of refraction. Thallium remains in solution on cooling and does not segregate at crystallization centers as did the silver.

(4) Liesegang Rings

Liesegang rings were observed in some of the specimens containing the silver salts when heated above the softening point of the glass.

Figure 10 shows photographs of a specific case of diffusion from $AgNO_3$ as the original source at 900°C. for 12 hours. The magnification is 9.2 times. *A* was taken with transmitted light using Wratten filters, D and H; *B* was taken with ultraviolet illumination.

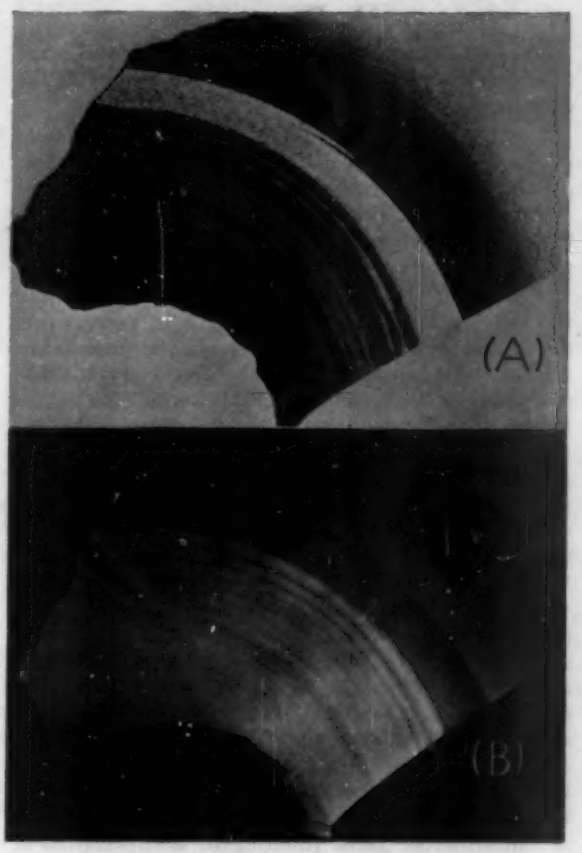

FIG. 10.—Liesegang rings in sample with $AgNO_3$ as source of diffusion at 900°C. for 12 hr., ×9.2; (*A*) transmitted light with D and H filters; (*B*) ultraviolet light.

The yellowish fluorescent areas in *B* appear as the lighter portions, and the darker portions represent areas of absorption or nonemission. The Liesegang rings appear in the grayish area, corresponding to area (3) (see section IV (1*F*), p. 273).

Though this phenomenon had appeared in several tests for all of the silver salts, it was not simple to reproduce. Inasmuch as no impurities were introduced, the rings, theoretically, should appear with variation either in the cooling or heating schedule. Samples were accordingly prepared, and the cooling was varied as follows: (1) cooling with the furnace and holding at 600°C. for one hour with no appearance of well-defined rings and (2) a heating cycle whereby the temperature was held at 600°C. with better defined rings.

It was not possible, however, in the time available to reproduce this condition which had appeared more or less accidentally. At some point during the long constant-temperature period, it was assumed that a drop in temperature actually occurred for a short time. In the grayish portion of the diffusion, the concentration of silver particles probably is such that aggregation occurs readily and any thermal disturbance would cause a departure from uniformity.

V. Discussion

The occurrence and rate of diffusion depends on the glass composition as well as on the salt to provide the diffusing particles.

The flint glass permitted diffusion, but a few samples of glass high in silica did not do so under the same conditions. The types of diffusion present are (1) replacement of alkali ions within the glass and (2) penetration of particles of some kind into the "holes of the glass."

Type (1) is present at all times, providing ions from the salt are available, and this type in general predominates for cases occurring at temperatures below the softening temperature of the glass. Type (2) is commonly present, usually in addition to type (1), at temperatures above the softening point. The expansion of the glass and the breaking of bonds in the glass structure form openings for the passage of larger particles. In a pure silica glass, for instance, type (2) diffusion would be the only kind present and consequently would be slow and would occur at elevated temperatures.

The source of diffusing particles is a controlling factor in the diffusion process. At temperatures below the softening point of glass, the salt must provide simple cations. Complex ions, however, may also penetrate into the surface layers a short distance. Diffusing ions from the salt at the test temperature can be provided in one of the following ways: (*a*) sufficiently high ionization constant of molten salt, (*b*) sufficiently high vapor or dissociation pressure, and (*c*) reaction of salt with the glass, resulting in the formation of cations. After their formation, the ions must be of such size as to penetrate into the glass openings. Those particles that enter the glass will have their rate of movement controlled by their effective size with the smaller moving the more rapidly.

Above the softening temperature of glass, the rate of diffusion increases because of the easier passage for the cations and also because larger complex ions and, perhaps, atoms are capable of penetration. The presence of complex forms is suggested by two conditions as follows: (1) With a salt containing oxygen, the oxygen content or pressure of the atmosphere affects the rate of diffusion and (2) cellular surfaces indicate movement of complex ions or molecules with subsequent decomposition or reaction in the glass.

It is apparent, therefore, that it is difficult to compare the ability of different salts to provide diffusing particles at a given temperature inasmuch as so many conditions are involved. Only a few of the salts tested, moreover, showed the occurrence of diffusion under the present experimental methods. Entirely different results, however, may be obtained if diffusion of a certain cation is promulgated from a different source; for example, when two glasses are in contact, with one already containing the diffusing ion and the other not.

The physical nature of the glass is important, and there are indications that the nature of diffusion changes at the critical temperature intervals, such as the softening point, and probably at the temperature at which an appreciable drop in viscosity occurs. Below the softening point, the movement of ions from the diffusion surface is slow as compared with the total ions in the surface concentration, and the average concentration of the silver in the diffused portion drops rapidly with increased distance of penetration. Above the softening point, the movement of particles through the glass is as rapid as their entrance, and there is no appreciable drop in average concentration with increased distance of penetration. This reduced resistance also facilitates the formation of aggregates or crystallites whose size depends entirely on the concentration of silver in the region, resulting in bands of different colors.

One of these areas of a given concentration is probably more sensitive to thermal effects than the others. This difference results in different states of aggregation, which in turn form additional bands resembling Liesegang rings. The theory is then proposed that rings in an experimental condition of this type are the result of a combination of a definite concentration and the presence of certain thermal conditions rather than the result of a precipitation caused only by supersaturation or reaction with the formation of a new salt.

VI. Summary

Of the salts tested, namely, $AgNO_3$, AgCl, Ag_2SO_4, Ag_2O, Cu_2Cl_2, $CuSO_4$, V_2O_5, $CrCl_3$, $PbCl_2$, Tl_2SO_4, $AuCl_3$, $PtCl_4$, Co_3O_4, and $FeCl_3$, those of silver, thallium, and vanadium diffused. The increasing order of ionic sizes is vanadium, silver, and thallium, which corresponds also approximately to the rates of diffusion. Copper salts showed a reaction with the glass with a possible diffusion. If that were the case, the diffusing particle probably was complex inasmuch as its apparent diffusion was much less than that for silver even though its cation is smaller than the silver cation.

The rate of diffusion for $AgNO_3$ at a given temperature is practically constant up to about 10 hours of test time and then decreases. In 36 hours, the distance of diffusion at 900°C. is 0.42 cm., and at 500°C., 0.05 cm.; AgCl at 900°C. is 0.8 cm.

The increase of diffusion for a given time with temperature rise is more rapid. A break is shown at the softening temperature, and another probably is present at the temperature of rapid decrease of viscosity.

Concentrations of silver from $AgNO_3$ with distance of diffusion show a sharp change at the softening temperature of the glass.

Fick's law (as generally given) holds only for a limited time at the beginning of the experiment; the so-called diffusion constant is therefore not constant throughout the entire test period.

The concentration gradient is a straight line approaching the distance axis asymptotically. The size of the particles in the colored bands in the specimens above the softening point, therefore, does not vary progressively because the number does not vary continuously.

In the gray diffused portion, Liesegang rings were found under certain experimental conditions.

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STRUCTURAL HOMOGENEITY OF GLASS*

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Abstract

A study of the mechanical strains present in a sample of glass does not insure a prediction of the future behavior of this glass. There is no simple relation between such strains and the physicochemical state of the glass. Most of these states, in fact, probably may be obtained with or without birefringence, depending on the thermal treatment to which the glass was submitted. If the glass is not in the equilibrium condition for the temperature at which it is being used, it will transform spontaneously toward that equilibrium. The birth and evolution of strains depend on these physicochemical unbalances as well as on other characteristics of the glass. Only the study of the physicochemical state can give reliable indications of the behavior of glass in practical use.

I. Introduction

In a previous paper,[1] a description was given of the behavior of glass during changes in temperature. The existence of a transformation region was emphasized, and the dependence of the behavior of glass on the thermal history was postulated from the study of the speed of transformation.

The present paper will consider the significance of these changes in properties of a glass in practical use, that is, (1) how they must be considered in annealing practice, (2) that more than just mechanical strain is involved, (3) that spontaneous variation may take place if a glass is not annealed to maximum density or maximum refractive index, and (4) by experiments conducted to amplify an understanding of the annealing process.

II. Fundamental Background

Reviewing the previous findings, Fig. 1 shows that when the refractive index (n) of a well-annealed borosilicate crown glass free from any strains was measured after holding at successive temperatures long enough to establish a constant value, a curve was obtained which consists of three regions. This curve indicates the following conditions:

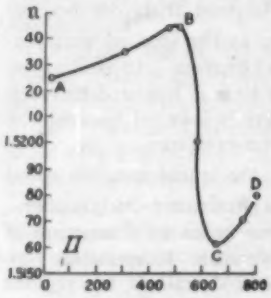

Fig. 1.—Variation of refractive index as function of temperature.

(1) Below a temperature, T_α, characteristic for each glass, the rate of change of n with T is approximately constant.† The variations of the refractive index are perfectly reversible in this region. No matter what the rate of heating or cooling, the final refractive index corresponding to each given temperature will always be the same when the entire sample has reached the selected temperature.

(2) Above a certain temperature, T_β, also characteristic for each kind of glass, the variation of the refractive index obeys the same laws as below T_α. The rate of change in refractive index is almost constant although the slope is not the same as in region (1). As far as

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[1] Aniuta Winter, "Transformation Region of Glass," *Jour. Amer. Ceram. Soc.*, **26** [6] 189–200 (1943).

† For all glasses mentioned in the reference on p. 278, $dn/dT > 0$. Pulfrich found that phosphate glasses exhibit negative values of dn/dT (see O. Pulfrich, *Ann. Phys Chem.*, **45**, 609 (1892)).

could be verified, the condition of reversibility is also satisfied.

(3) In the interval of temperatures between T_α and T_β, which will be called "the transformation region," the glass behaves quite differently. Starting from T_α, the refractive index changes abruptly and non-linearly up to T_β. It remains true that a definite characterizing refractive index corresponds to each temperature. But this value is reached only after the sample has been maintained at the chosen temperature during a lapse of time, which is determined by the temperature as well as by the initial state of the sample. As a result, glass within the transformation region can temporarily have an index different from its characteristic equilibrium value and dependent on its thermal history. This temporary index will not be stable but will vary spontaneously toward the equilibrium value.

If T is maintained constant,[1] this spontaneous evolution follows the empirical law of equation (1).

$$n = n_T + (n_0 - n_T)e^{-Bt} \qquad (1)$$

n_0 = refractive index at time, $t = 0$
n_T = index of equilibrium at temperature, T
B = parameter function of T but constant in relation to time

A study of B shows that the time to reach equilibrium within the precision of the measurement (1×10^{-3}) is practically nil at T_β, whatever the initial state. For other temperatures, this time depends on the extent of the difference between the initial and the equilibrium values; for any given difference, this time becomes shorter as the temperature comes closer to T_β.

A sample heated at T_β or beyond therefore reaches equilibrium at the same time as the studied temperature no matter what the rate of heating. In cooling, on the contrary, more and more time is required to reach equilibrium as the temperature is lowered because the transformation speed also becomes slower.

Except in the region of T_β, the transformation speed is so slow that it is possible to eliminate from consideration in the study of refractive index as a function of temperature all of the reversible temperature coefficient of n, which has been described for regions below T_α and above T_β.

It is sufficient to cool the glass rapidly after equilibrium has been assuredly reached at the chosen temperature, T_n, and to take the refractive index measured at room temperature as the value belonging to T_n. By using small samples, the cooling throughout takes place in such a short time that only the changes resulting from the reversible component can be accomplished whereas no appreciable transformation toward the room-temperature value can take place except for T_n very near to T_β.

The curve of Fig. 2 (A) was obtained in this manner.[2] Note that the refractive index keeps the same value, n_α, for all temperatures below T_α; the same value, n_β, for

[1] This type of curve was first described by A. A. Lebedeff, *Rev. Optique*, **5**, 1 (1926).

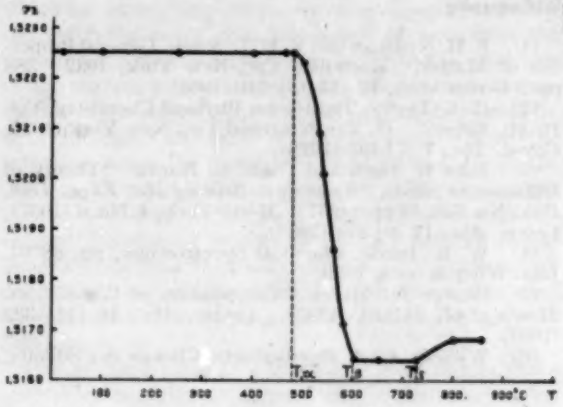

FIG. 2(A).—Variation of refractive index as function of heat-treatment.

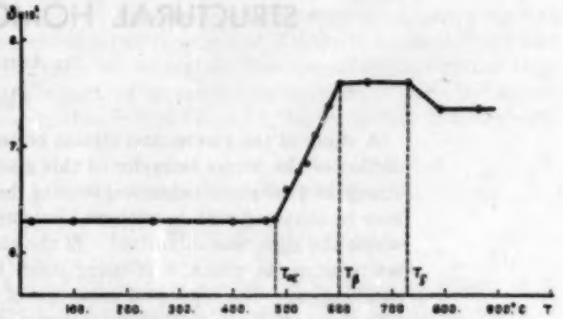

FIG. 2(σ).—Variation of expansion coefficient as function of heat-treatment.

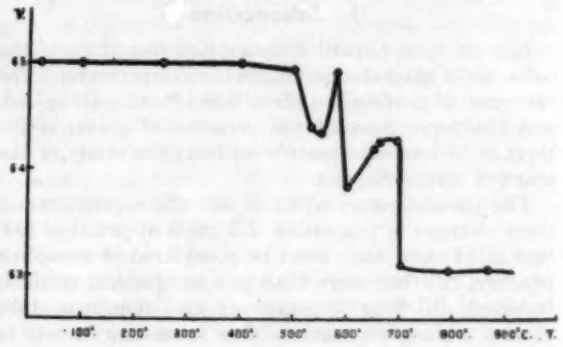

FIG. 3.—Variation of dispersion as function of heat-treatment.

temperatures above T_β; and is variable only in the transformation region.* (The hook at the temperature marked T_s will be discussed later.)

The writer has adopted the practice of using the term "alpha glass" for any glass in equilibrium for any temperature below T_α. The refractive index values at differing temperatures within this region vary only by the reversible component; if it is abruptly cooled

* Analogous curves were obtained on the other glasses such as the dense and light barium crown types, the extra dense, dense, and light flints, ordinary crown, baryta flint, and fluor-crown.

to room temperature, the glass will always have the same refractive index no matter what the initial temperature. "Beta glass" is that glass which is in equilibrium at any temperature above T_β. In the transformation region, there will correspond to each temperature a different refractive index or "state" of the glass intermediate between the alpha and beta states. For this borosilicate crown glass, $\Delta n = n_\alpha - n_\beta = 610 \times 10^{-5}$, and this was found to vary from 210×10^{-5} for a light flint to 650×10^{-5} for a dense barium crown.

The curve in Fig. 2 (*B*) shows the coefficient of expansion measured between 20° and 50°C. on the quenched samples used for the corresponding refractivity measurements. T_α and T_β can also be distinguished from the measurement of this physical property as well as the regions for alpha glass, beta glass, and transformation.

$$\Delta\delta = \delta_\beta - \delta_\alpha \text{ is about } 30\% \text{ of } \delta_\alpha$$

For optical calculations, the property, $\nu = n_D - 1/n_F - n_C$, is also very important. Figure 3 shows ν as a function of temperature for the samples of Fig. 2. In the transformation region, ν passes through a series of maxima and minima at temperatures differing only slightly from each other. Thus if a sample is not well annealed so that the refractive index remains in the transformation region domain, a very small change in the annealing process may produce a large variation in ν. This means that ν cannot be predicted but should be determined separately for each specimen.

The glass used for the experiments was originally annealed very well. The curve of Fig. 1 was drawn from measurements made when the glass was inside the furnace at increasing temperatures. Strains, therefore, could not appear, and the phenomena described are completely independent of strain. As for the data of Figs. 2 (*A*) and 2 (*B*), strains do not appear below a temperature, T_s, appreciably higher than T_β, as proved by direct observation with polarized light. This permits a comparison of (1), which is the variation between n_α and n_β, which is independent of strain, with (2), which is the refractive index change produced by the occurrence of strains at T_s, represented by the break in the curves of Fig. 2 at T_s.

It can be seen that strains here produce an increase in refractive index whereas the temperature rise from T_α to T_β leads to a decrease. The difference, $n_\alpha - n_\beta$, moreover, is 610×10^{-5}, whereas the increase in refractive index caused by strain is only 20×10^{-5}. Much more significant effects result from the transformation phenomena than from any strains caused by rapid cooling.

All of these observations are consequences of the fundamental fact already mentioned, but because of its importance it is now restated more precisely. A sample of glass taken from a state of equilibrium at a temperature, $T_i > T_\alpha$, and cooled down reaches its final temperature, $T_f (< T_i)$, in a state of equilibrium if, and only if, the cooling operation is conducted with a speed equal to or smaller than that imposed by the laws of transformation. When these rules are not observed, the state of glass lags behind the temperature, and while the temperature has reached its final value, T_f, the state of glass still corresponds to the state of equilibrium at temperature τ situated in the transformation region between T_i and T_α.[3]

A glass at T_f having physical property values corresponding to τ cannot remain permanently in this condition and will continue to transform itself toward values stable at T_f. It will tend to increase, for example, in refractive index until n_α, if T_f has any value lower than T_α. Left at T_f, the glass will transform spontaneously.

This spontaneous variation would be important in practice even if it affected only the refractive index. The coefficient of expansion and the specific volume of the glass, however, change at the same time. In a perfectly homogeneous specimen, these changes would provoke a shrinkage in dimensions without altering the shape. The newly cooled glass, in practice, does not have the same temperature throughout its mass, and different portions of the sample will be transformed in an unequal manner, that is, the sample will be heterogeneous.

During the evolution from low to high refractive index, such heterogeneity will diminish in time because those portions further from the equilibrium state transform more rapidly. The specific volume changes at the same time but in a different way at different points. Strains appear between different parts of the sample without its being submitted to any variation of the temperature. Such strains, which will be called physicochemical, may become great enough to provoke spontaneous breakage of the glass, a phenomenon hitherto unexplained.

Sometime before the breaking occurs, the strains should cause a deformation of the surface. That this deformation does, in fact, take place was verified by a direct experiment in conjunction with another, which shows the consequence of the differences between the coefficients of expansion at different portions of the glass.

Until the present time, it has been supposed that the glass is maintained at a constant temperature so that any deformation was the result of the spontaneous changes in the specific volume. If the glass, in addition, is submitted to a temperature change, the variability in the coefficient of expansion between different parts will produce additional strains and deformations.

It is essential to distinguish the physicochemical strains from the mechanical strains. The latter appear when the cooling sets the outer layers of the glass while the inside mass is still "pasty." The interior is prevented from contracting when it in turn cools, and mechanical strains appear. One characteristic in which the two kinds of strain differ is that after the entire mass of glass has taken the final temperature, the mechanical strains remain constant.

[3] Tool refers to τ as the "fictive" temperature; see A. Q. Tool, "Analytical Representation Concerning Glass in Its Glass Annealing Range," abstracted in the program issue for the Fourty-Fourth Annual Meeting of The American Ceramic Society, April 15, 1942; *The Bulletin* (Program Section), 21 [4] p. 13.

III. Practical Consequences

Some of the experiments which show the significance in glass practice of the phenomena already described will be discussed. A particular effort will be made in each case to separate the role of physicochemical heterogeneity from that of mechanical strains.

The defects generally attributed to a rapidly cooled glass may be classified as follows: (1) double refraction, (2) instability with time, that is, aging (attributed to spontaneous variation of the surface), (3) spontaneous breakage, and (4) variation in refractive index from one portion of the glass to another; because this distribution will also vary spontaneously with time, it correlates with the aging effect in (2). Inasmuch as double refraction (1) and its effects are well known, only the other three will be discussed, chiefly in relation to optical glass.

(1) Deformation of Surface

To study this defect, samples of glass were used in the form of plates, 120 mm. in diameter and 30 mm. thick. The glass was taken from the same melt of borosilicate crown previously mentioned and was well annealed at the beginning of the experiment. Inasmuch as the effects of strains are to be differentiated from those of physicochemical constitution, the distribution of strains and of refractive index was first measured.

Examined under the crossed Nicols, the two plates showed no color and practically no strain was present. Examined in a Michelson interferometer* through the 120-mm. thickness, the plates showed (at a wave length of 546 millimicrons) a number of fringes corresponding to the variation in refractive index of 3×10^{-5}. Examined through the flat faces (30-mm. thickness), optical flatness was observed.

Measurements of refractive index on the surface by limit refraction method confirmed these results.

The two plates were left in contact with each other for six months at room temperature. The character of the surface was checked by observing the fringes given by the layer of air between the two flat surfaces. Because this technique checks not the flatness of a single surface but the average of the two flats, any deformation which exists may be compensated. To make sure that this could not occur, the two flats were separated and the condition of each was compared with a third plate of identical glass.

The results were the same in all of these experiments, that is, the surface remained constant within the precision of the experiment, 0.1 fringe.

The plates were then placed in a thermostatically controlled oven, and the character of the surface was checked when the sample had reached an equilibrium of temperature or various selected temperatures between 20° and 100°C. Although this range of temperatures is broader than optical glass encounters in practical use, the exaggeration makes the behavior more evident.

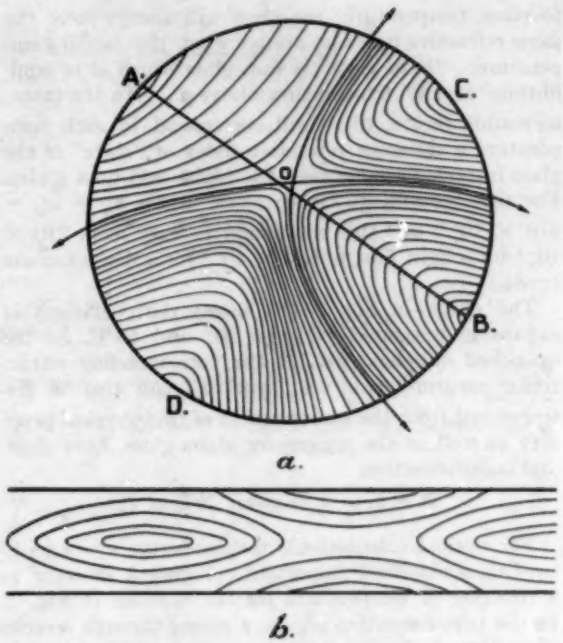

FIG. 4.—Appearance of test plate examined in interferometer by immersion method; (*a*) observed through flat surfaces and (*b*) observed through thick section.

The results were the same as before. At each temperature level, the surfaces resumed their previous form as soon as any differences of temperature in the mass of the glass were smoothed out. This proves that the surface of a well-annealed glass does not change under ordinary conditions of use.

One of the plates was next heated in an electric furnace to 650°C., held there for six hours, and cooled to room temperature at a rate of 1°C. per minute in a current of air. After equalization of temperature throughout the plate, the distribution of strains and refractive indices was again measured.

In polarized light, a black cross, almost stationary, appeared when the sample was revolved; the strain distribution was symmetrical within the plate. The birefringence varied from $n_0 - n_e = 9 \times 10^{-7}$ in the center to 200×10^{-7} at the edges.

Examined in the interferometer by the immersion method, the plate appeared as shown in Fig. 4. In the section parallel to the flat sides, the lines of equal refractive index are hyperboles (Fig. 4 (*a*)). The refractive index increases continuously from *A* to *B* and decreases from *O* to *C* and from *O* to *D*. The direction of the air draught is from *A* to *B*, whereas the two sections *OC* and *OD* are probably the result of the reflection of air at the wall of the furnace. Along the asymptote, the variation of the refractive index of course is nil.

Between *A* and *B*, the number of fringes for $\lambda = 0^{\mu}.546$ is 165 so that $\Delta n = 150 \times 10^{-5}$ from *A* to *B*.

* All tests with the Michelson interferometer were made by an immersion method to avoid special and very difficult polishing of the glass. The specimen was immersed in a cell specially prepared for this purpose and filled with a mixture of carbon tetrachloride and carbon disulfide in such proportions that the refractive index exactly matched that of the glass.

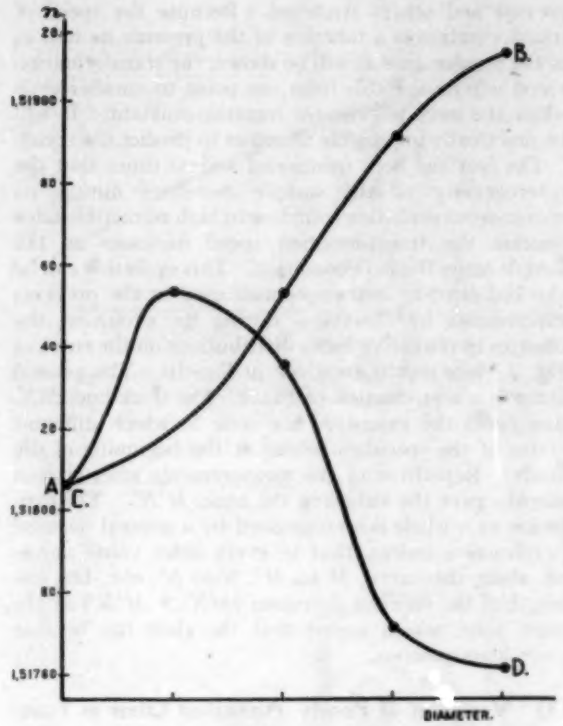

FIG. 5.—Results of refractive index measurements along *AB* and *CD* diameters on surface.

All of these results are completely confirmed by direct measurement of the refractive index at the surface. Measurements at the surface give only 104×10^{-6} for $\Delta n = n_B - n_A$, but this lack of agreement with the value previously found is to be expected inasmuch as the refractive index varies abruptly around point *A*, and it is almost impossible to measure the true index at this point.

When observed through the thick section in a direction parallel to the flat sides, the lines of equal refractive index appear as elliptical fringes (Fig. 4 (*b*)). The surfaces of equal refractivity thus resemble a hyperboloid with two surfaces (the orthogonal sections are, respectively, a hyperbole and an ellipse). Figure 5 represents the results for the refractive index measured on the surface along the diameters, *AB* and *CD*.

The shape of the surface of this plate after cooling was checked by observing the fringes produced by the air film between this plate and the well-annealed sample. Because the annealed plate has been proved stable within the limits of the experiment, all deformation observed must be the result of the cooled plate. The two plates at first were left at room temperature (20°C.) for three months. Several profiles of the surface were drawn as they appeared from the distribution of the fringes. A small deformation was found along the diameter, *AB*, as shown in Fig. 6.

Then, as with the well-annealed glass, the condition of the surface was studied at different temperature levels between 20° and 100°C. This time it was found that when the glass is once heated, the surface

FIG. 6.—Deformation of surface along diameter *AB* after test plate was maintained 3 months at room temperature.

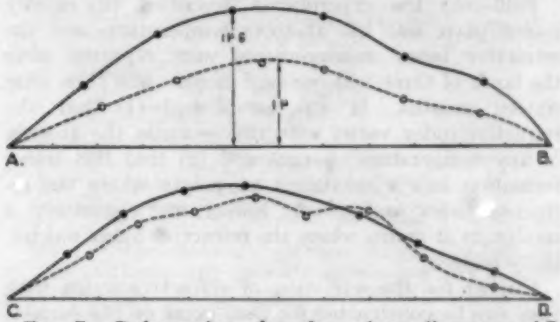

FIG. 7.—Deformation of surface along diameters *AB* and *CD* after test plate was heated several times up to 010° C.

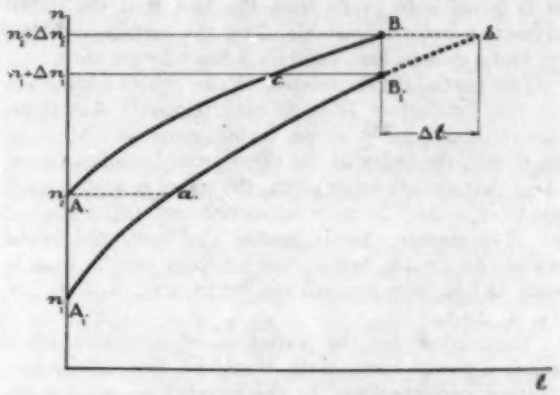

FIG. 8.—Two curves of variation of refractive index with time relative to two points somewhere on surface.

never recovers its initial form. Not only is this form different at every temperature, but different forms are present even at the same temperature after a return from a temperature change. The condition of the surface varies in an irreversible manner and depends entirely on the thermal history.

The heating and cooling between 20° and 100°C. was repeated several times, and profiles were drawn after each heating to check any changes in the surface at return to room temperature. Maximum deformation was observed at the diameter, *AB*, and minimum, at *CD*. Figure 7 represents these two profiles as they appeared at the start and then after several heatings.

At the end of the experiment, the birefringence was measured again and was found to have retained the initial value within the precision of the measurement ($\delta = 0.004\ \lambda$). Thus no relation exists between the variation of shape and the distribution of strains. Instead, the form of the surface varies most along the line of greatest physicochemical heterogeneity and least along the most homogeneous diameter. The deformation seems to be entirely the result of the physicochemical heterogeneity of the glass. The lack

of reversibility, moreover, which has previously been emphasized in speaking of the influence of temperature changes on the refractive index, indicates once more the connection between both of these phenomena.

(2) Spontaneous Transformations

Following the experiments described, the rapidly cooled plate was left at room temperature, and the refractive index measurements were repeated after the lapse of three and one-half months and then after sixteen months. It was established (1) that the refractive index varies with time even in the absence of any temperature changes and (2) that this transformation has a maximum at points where the refractive index was initially lowest, and conversely, a minimum at points where the refractive index was initially highest.

Curves for the variation of refractive index with time can be constructed for each point on the surface. Although direct data are available only for the time interval during which the glass was under observation, it is possible to profit from the fact that the initial refractive index is variable along the surface and thus to find a general law, valid for a much longer time.

Two partial curves relative to two points somewhere on the flat surface (Fig. 8) may be used. Let n_1 be the refractive index at one certain point at a time, t_0; at time t, the index at the same point becomes $(n_1 + \Delta n_1)$. At an adjoining point, the index n_2 at t_0 is such that $(n_1 + \Delta n_1) > n_2 > n_1$, n_2 becomes $(n_2 + \Delta n_2)$ at t. The change, Δn, is greater the lower the initial value, $\Delta n_1 > \Delta n_2$, but n_1 changes more rapidly than n_2 only as long as it remains smaller than n_2, $(n_2 + \Delta n_2) > (n_1 + \Delta n_1)$.

The curves for the variation of refractive index relative to the two points, therefore, have a common portion corresponding to the interval n_2, $n_1 + \Delta n_1$ (aB_1 and Ac in Fig. 8). It was proved directly that the two parts can be superposed by a translation parallel to the time axis, whatever the chosen values of n_1 and n_2. This result indicates that the different curves represent arcs of the same general curve or, in other words, the index changes everywhere follow the same general law. By translation of the partial curves to bring in coincidence the parts having a common ordinate, a general curve has been obtained which can be extended to a longer time interval (Fig. 9).

It was to be expected that the curves for different points in the glass are arcs of the same general curve because the curve of Fig. 9 is only a particular case of the transformation of beta to alpha glass, thus following the general law as given in section II.

$$n = n_\alpha + (n_0 - n_\alpha) \cdot e^{-Bt} \qquad (2)$$

$n_T = n_\alpha$ in this case because $T < T_\alpha$

It must be emphasized that the empirical determination of coefficient B is valid only for the given sample or for samples which are exactly identical with it because of the strained condition that may appear during the rapid cooling or spontaneously after the glass has reached the final temperature. Whatever the origin of strains in the glass, certain parts are compressed and others stretched. Because the speed of transformation is a function of the pressure as well as of the temperature as will be shown, the transformation speed will be variable from one point to another even when the outside pressure remains constant. It will be practically impossible therefore to predict the speed.

The fact has been mentioned several times that the heterogeneity of the sample decreases during its spontaneous evolution from low to high refractive index because the transformation speed increases as the sample nears the beta condition. This evolution can be checked directly on the specimen used in the previous experiments by observing, during the evolution, the changes in refractive index distributions on the curve of Fig. 2; these results are given in Fig. 10. The general curve is a reproduction of Fig. 2. The thick line, MN, designates the extent of the zone to which different states of the specimen belong at the beginning of the study. Repetition of the measurements after sixteen months gave the values in the zone, $M'N'$. The evolution as a whole is accompanied by a general increase in refractive index; that is, every index value moves up along the curve, M to M', N to N', etc., but the length of the segment decreases ($MN > M'N'$) at the same time, which means that the glass has become more homogeneous.

(3) Variation of Poorly Annealed Glass as Function of Temperature

The following experiment will show the importance of the physicochemical structure of glass in applications other than precision optics.

A radio-tube factory complained that certain bulbs broke for no apparent reason; the glass had been checked by the usual method of disappearance of birefringence strain and came within the standards of good annealing.

The physicochemical state of this glass was determined by the method of quenched samples previously described.[1] Instead of obtaining curves analogous to those of Figs. 2 (A) and 2 (B), which are characteristic for well-annealed glass, the curves shown in Fig. 11 were obtained. The refractive index as well as the coefficient of expansivity started from a value indicating that the glass was initially almost entirely in the beta state. No noticeable changes were observed before the glass reached temperatures at which the speed of transformation was fast enough to produce an effect during the short time of the experiment (T_A in Fig. 11). Starting here, the glass tended to transform to the alpha state, which is the stable condition for this temperature region. With further increase in temperature, the region where beta glass is stable was approached. The actual state of the glass and the equilibrium state corresponding to these momentary temperatures tended toward each other until they coincided at the temperature, T_N. From this moment, the specimen behaved like well-annealed glass and tended to the beta state. Beginning at T_N, the curves resemble those of Fig. 2. The breaks mark the appearance of mechanical strains.

A new method was introduced for checking the

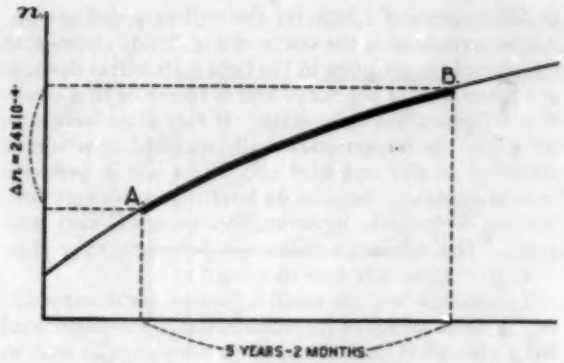

FIG. 9.—General curve of variations of refractive index with time.

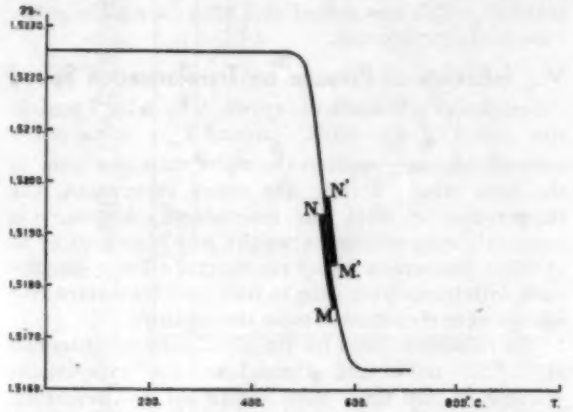

FIG. 10.—Changes in refractive index distribution after 16 months of experiment.

physicochemical homogeneity of the radio tubes, and the percentage of broken ware decreased considerably.

IV. Physicochemical State of Glass versus Strains

The example described shows once more that removal of birefringence is not enough to prevent the inconveniences of rapid cooling. Two points must always be kept in mind during the annealing process, namely, (*a*) removal of mechanical strains, for which the general method was indicated by the classic work of Adams and Williamson,[4] and (*b*) physicochemical homogeneity, which is quantitatively more important. To bring about adequate homogeneity, the annealing has to conform to the methods deduced from the laws governing the transformation rate.

It must be emphasized that these two processes can be largely independent of each other. To prove their complete independence, the existence of glass should be shown in each of the following forms or conditions: I, entirely in the alpha state and practically free from strains; II, entirely in the alpha state but with strains;

[4] See L. H. Adams and E. D. Williamson, *Phys. Rev.*, **14**, 99 (1919); *Jour. Wash. Acad. Sci.*, **11**, 609 (1919); "Annealing of Glass," *Jour. Franklin Inst.*, **190**, 216, 597–631, and 835–70 (1920); and *Jour. Optical Soc. Amer.*, **4**, 213 (1930).

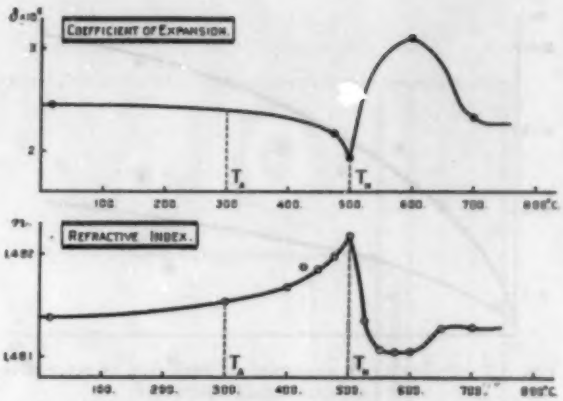

FIG. 11.—Variations of coefficient of expansion and refractive index of poorly annealed glass as function of heat treatment.

III, entirely in the beta state without strains; and IV, entirely in the beta state with strains.

Glass in form I is the most suitable for optical use. That it can be prepared is proved by the fact that the sample used to obtain the curves of Figs. 1 and 2 was free from strain.

Although the glass in form IV is very poor for optical uses, it is the most easily obtained. Such glass was prepared by rapid melting and quenching and used for studying the hook shown in the curves of Figs. 2 and 11.

A specimen of glass in form III was also prepared. This glass confirms the statement that the removal of strain is not necessarily simultaneous with production of physicochemical homogeneity. The question, however, of their complete independence remains, or must a completely homogeneous alpha glass be strain-free; that is, can glass exist in form II?

For preparation of a sample in form II, glass should be left to itself. A glass that has not been entirely transformed to the alpha state is not stable at room temperature and it spontaneously tends to this state. If this sample, furthermore, is not homogeneous, strains are produced with aging which are the result of unequal changes in specific volume at different places even when none existed initially. Two different nonhomogeneous samples, one with strains and the other without strains, are kept at room temperature, and observations of their transformations with time will show whether it is possible to produce glass in form II.

The samples used for this experiment were (1) the rapidly cooled plate referred to in Fig. 9 and (2) the sample in form III to be described. Rough calculations, made by extrapolating the curve of Fig. 9, indicate that the time needed for this experiment would be at least fifty years. Measurements actually have been carried on for five years, and the definite results are not yet known.

Form III obviously can be obtained at any sufficiently high temperature at which the beta state is in equilibrium. At room temperature, however, it is possible to obtain a glass in a state only approximating the beta condition because the transforma-

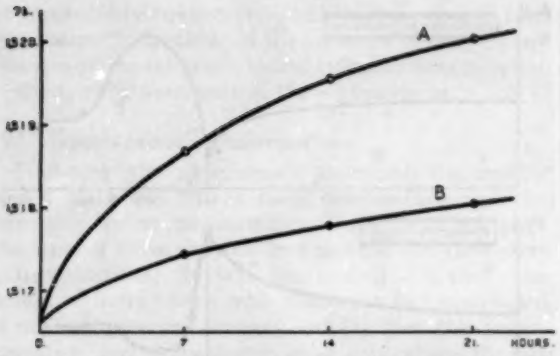

FIG. 12.—Influence of pressure on variation of refractive index at constant temperature.

tion at T_β is practically instantaneous. The method for obtaining such beta glass without strains will be described in detail, because the existence at room temperature of a form very near to III always provokes surprise and incredulity although the existence of glass in forms I and IV has long been acknowledged.

To prepare a strain-free beta glass, a strain-free sample is heated to the temperature T_β. The glass is certainly in the beta state at this temperature because the transformation is practically instantaneous. From T_β, the sample is cooled (so quickly that no appreciable transformations can occur) to a temperature, T_l, at which the transformation speed is so low as to be of no importance during the remainder of the operation. The laws governing the transformation give 50°C. for this cooling range $(T_\beta - T_l)$. The resulting temperature gradient will be small enough not to introduce much strain. The interval, $T_\beta - T_l$, is small, and it becomes possible to obtain form III because from T_l to room temperature the cooling can be slow enough to avoid any birth of strain, if such a possibility still should exist.

This experiment was performed with a borosilicate crown. A sample of well-annealed glass, 20 × 10 × 5 mm. in size, was first checked in a polariscope for freedom from strain and then divided into two parts, one being kept for reference. The curve of Fig. 2 gives 600°C. for a practical T_β,* and T_l will be 550°C. This cooling was obtained by throwing the glass into a lead bath at T_l. After it was certain that the sample was entirely at T_l, the lead was siphoned off and the rest of the cooling conducted at a selected rate.

Following this thermal treatment, the sample was examined again under crossed Nicols. Very little light was transmitted, but the birefringence was too small to be measured with the compensator that was used; the path difference was below $\delta = 0.004\,\lambda$.

The glass was polished after cooling, and it is interesting to note that the polishers did not notice any special difference in the way the glass took grinding and polishing.

The refractive index was now 1.5167 for λ = 0$^\mu$.546 in place of 1.5226 for the well-annealed sample. A comparison with the curve of Fig. 2 (*A*) shows that this sample is not quite in the beta state but is down at the lower part of the curve and is therefore in a condition adjoining the beta state. If this glass were submitted to the inspections usually specified, it would be classified as well annealed and fit for use in precision optical apparatus because its birefringence is very low; it is not so suitable, however, because it will vary with time. The refractive index was found to have risen 4×10^{-5} after only four months.

This sample was too small to be used for direct study of the deformation of its surface, but a lens fabricated from this glass had changed in focal length and in aberrations after one year of aging.

Measurements on the other (the reference) half of the original sample proved that its refractive index was perfectly stable and stayed at 1.5226 during the entire time of the experiment.

V. Influence of Pressure on Transformation Speed

Samples of a borosilicate crown, 5 by 5 by 1 mm. in size, were heated to 490°C. (around T_α). Some of the samples originally were in the alpha state and some in the beta state. During the entire experiment, the temperature of 490° was maintained constant. On some of these samples, a weight was placed so as to obtain a pressure of 20 kg. per sq. cm. These samples were withdrawn from time to time, and their refractive indices were measured at room temperature.

The refractive index for the alpha samples remained at 1.5223 unchanged throughout the experiments whether or not they were submitted to weighting. The pressure, however, accelerated the transformation of the beta samples, as may be seen from Fig. 12. The refractive index of the beta samples was 1.5162 at the start of the experiment. This index reached 1.5201 after 21 hours at 490° for the loaded samples (curve *A*). For the unloaded samples (curve *B*), this index reached 1.5178 after the same time.

VI. Conclusions

Study of the mechanical strains present in a sample of glass does not enable prediction of the future behavior of this glass. There is no simple relation between such strains and the physicochemical state of the glass. Most of these states in fact can be obtained with or without birefringence, depending on the thermal treatment to which the glass was submitted.

If the glass is not in the equilibrium condition for the temperature at which it is being used, it will transform spontaneously toward that equilibrium. The birth and evolution of strains depend on these physicochemical unbalances as well as on other characteristics of the glass. Only the study of the physicochemical state can give reliable indications of the behavior of glass in practical use.

Acknowledgment

It is a pleasure at this time to thank A. G. Pincus of the American Optical Company for his many valuable suggestions as well as for his help in the English correction of this paper.

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* The true T_β given by Fig. 1 is higher, but the transformation speed is too great to permit retaining this state at room temperature.

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